U.S. DEPARTMENT OF COMMERCE PB80-166622

Advanced Filtration of Pulp Mill Wastes

International Paper Co.
Mobile, AL

Prepared for

Industrial Environmental Research
Lab.-Cincinnati, OH

Dec 79

U.S. Department of Commerce
National Technical Information Service
NTIS

United States
Environmental Protection
Agency

Industrial Environmental Research
Laboratory
Cincinnati OH 45268

EPA-600/2-79-209
December 1979

PB80-166622

Research and Development

EPA

Advanced Filtration of Pulp Mill Wastes

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TECHNICAL REPORT DATA

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1. REPORT NO. EPA-600/2-79-209	2.	3. RECIPIENT'S ACCESSION NO. PB80-166622
4. TITLE AND SUBTITLE ADVANCED FILTRATION OF PULP MILL WASTES		5. REPORT DATE December 1979 issuing date
		6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) John T. McKinnon		8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS International Paper Company Science and Technology Division—ERRL P. O. Box 2787 Mobile, Alabama 36601		10. PROGRAM ELEMENT NO. 1BB610
		11. CONTRACT/GRANT NO. R 803667–01–1
12. SPONSORING AGENCY NAME AND ADDRESS Industrial Environmental Research Laboratory Office of Research and Development U. S. Environmental Protection Agency Cincinnati, Ohio 45268		13. TYPE OF REPORT AND PERIOD COVERED Final 4/28/75–2/27/78
		14. SPONSORING AGENCY CODE EPA/600/12

15. SUPPLEMENTARY NOTES

16. ABSTRACT

Laboratory and pilot plant studies of reverse osmosis (hyperfiltration) and ultrafiltration of pulp mill wastes were performed by International Paper Company and Oak Ridge National Laboratory (subcontractor). Decker filtrates were treated with dynamically formed reverse osmosis membranes consisting of hydrous zirconium (IV) oxide and polyacrylic acid. Bleach plant caustic extraction filtrate (E_1) was treated with dynamically formed ultrafiltration membranes consisting of hydrous zirconium (IV) oxide and hydrous silicon (IV) oxide.

The units demonstrated that a properly designed system could effectively treat pulp mill wastewaters to reduce pollution loads and provide recycleable permeates. Mechanical difficulties prevented the accumulation of sufficient data for scale-up calculations, but the experience obtained will be useful to future work involving dynamic membrane systems.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
circulation*, color, membranes*, osmosis*, pulp mills*, waste water, water pollution	Hyperfiltration, Mott porous steel tubes, permeates, reverse osmosis, Selas porous ceramic tube bundles, ultrafiltration, Union Carbide porous carbon tubes, UCARSEP™	13B

18. DISTRIBUTION STATEMENT RELEASE TO PUBLIC	19. SECURITY CLASS *(This Report)* UNCLASSIFIED	21. NO. OF PAGES
	20. SECURITY CLASS *(This page)* UNCLASSIFIED	22. PRICE

EPA Form 2220–1 (Rev. 4–77) PREVIOUS EDITION IS OBSOLETE

☆ U.S. GOVERNMENT PRINTING OFFICE 1980-657-146/5560

EPA-600/2-79-209
December 1979

ADVANCED FILTRATION OF PULP MILL WASTES

by

John T. McKinnon
International Paper Company
Mobile, Alabama 36601

Grant No. R803667-01-1

Project Officers

Donald L. Wilson and Ralph H. Scott
Food and Wood Products Branch
Industrial Environmental Research Laboratory
Cincinnati, Ohio 45268

Industrial Environmental Research Laboratory
Office of Research and Development
U. S. Environmental Protection Agency
Cincinnati, Ohio. 45268

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FOREWORD

When energy and material resources are extracted, processed, converted, and used, the related pollutional impacts on our environment and even on our health often require that new and increasingly more efficient pollution control methods be used. The Industrial Environmental Research Laboratory – Cincinnati (IERL–Ci) assists in developing and demonstrating new and improved methodologies that will meet these needs both efficiently and economically.

This report is a summary of laboratory and pilot plant studies of reverse osmosis (hyperfiltration) and ultrafiltration of pulp mill waste waters using dynamically formed (or dynamic) membranes. Although the results obtained were not sufficient to provide scale-up data for such systems, the studies did provide useful information that will aid the progress of future work. The operating experience with the pilot units should be especially beneficial to the design of future systems, as most of the difficulties encountered, both mechanical problems and membrane problems, could be eliminated with redesigned equipment. This report will be valuable to researchers interested in the treatment of industrial waste waters with membrane systems. Tubular dynamic membrane systems have the potential of greater flexibility and operating efficiency under more extreme conditions than the conventional precast membranes. Persons concerned with in-plant treatment of pulp mill waste waters should be especially interested in this study, as the pilot plant operating data are indicative of the removal efficiencies of the dynamic membrane units now appearing on the market. For further information, please contact the Food and Wood Products Branch of the Industrial Environmental Research Laboratory, Cincinnati, Ohio.

David G. Stephan
Director
Industrial Environmental Research Laboratory
Cincinnati

ABSTRACT

This report covers the experimental development and the pilot plant operation of dynamically formed reverse osmosis and ultrafiltration membranes for the treatment of highly colored waste waters. The dynamic membranes were formed on porous supports typically having pores in the submicron range. The dynamic membranes were made of substances added to solutions circulated under pressure past the supports. During the pilot plant testing, membranes were supported by porous ceramic and carbon tubes in an outside flow arrangement. A hydrous zirconium (IV) oxide-polyacrylic acid membrane was used in the reverse osmosis mode to treat a pulp mill decker filtrate. A hydrous zirconium (IV) oxide-silicon (IV) oxide membrane was used in the ultrafiltration mode to treat a bleach plant caustic extraction filtrate (E_1).

During the pilot plant operation, the reverse osmosis unit treated the decker filtrate to a reusable quality and the ultrafiltration unit was able to concentrate the bleach plant waste water to a solids concentration of greater than 10%. Both units achieved better than 98% color removal and high levels of organic compound removal. The ultrafiltration unit was capable of fluxes of 4.07 $m^3/m^2/d$ (100 gfd) or higher, and the reverse osmosis unit produced fluxes in excess of 1.63 $m^3/m^2/d$ (40 gfd).

The membranes used in this pilot plant study, which are not commercial membranes, showed a relatively high degree of instability and variability. Mechanical and design problems precluded the gathering of enough data for a scale-up or an economic evaluation. More development work is required to eliminate the operational problems and to determine the membrane life.

This report was submitted in fulfillment of Grant No. R803667-01-1 by International Paper Company under the partial sponsorship of the U. S. Environmental Protection Agency. This report covers a period from August 1, 1976 to April 28, 1978.

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ABBREVIATIONS, SYMBOLS, AND METRIC CONVERSIONS

ABBREVIATIONS

BOD_5 -- biochemical oxygen demand, 5-day test
COD -- chemical oxygen demand
TOC -- total organic carbon
% R -- percent rejection of constituent
gfd -- gallons per square foot per day
$m^3/m^2/d$ -- cubic meter per square meter per day
Pa -- Pascals (Newtons per square meter)
psi -- pounds per square inch
psig -- pounds per square inch gauge
m^3/s -- cubic meter per second
gpm -- gallons per minute
m/s -- meters per second
ft/sec -- feet per second
ppm -- parts per million
c.u. -- color units
μm -- micrometers (microns)

SYMBOLS

E_1 -- bleach plant caustic extraction filtrate
HNO_3 -- nitric acid
H_2SO_4 -- sulfuric acid
J -- flux rate
NaOH -- sodium hydroxide
$NaNO_3$ -- sodium nitrate
NaCl -- sodium chloride
$NaHCO_3$ -- sodium bicarbonate
Na_2CO_3 -- sodium carbonate
Na_2SO_4 -- sodium sulfate
Zr(IV) – PAA -- hydrous zirconium(IV) oxide – polyacrylic acid
Zr(IV) – Si(IV) -- hydrous zirconium(IV) oxide – silicon(IV) oxide
$Zr(NO_3)_4$ -- zirconium nitrate

METRIC CONVERSIONS

MULTIPLY	BY	TO OBTAIN
gfd	4.074×10^{-2}	$m^3/m^2/d$
psi	6.8947572×10^3	Pa
ft/sec	3.048×10^{-1}	m/s
gpm	6.3088×10^{-5}	m^3/s
atm	1.0135×10^5	Pa

ACKNOWLEDGMENTS

The project was performed by International Paper Company, with Oak Ridge National Laboratory participation under subcontract OIC-SNN-29. Oak Ridge National Laboratory is a part of the U. S. Department of Energy and is operated by Union Carbide Nuclear Corporation. The assistance of Dr. J. S. Johnson, Jr., Dr. A. J. Shor, Mr. Gary Westmoreland, and Mr. Philip Hayes of Oak Ridge National Laboratory in performing the laboratory studies, constructing the pilot units, and providing technical support is gratefully acknowledged. The project manager for International Paper Company was Mr. Lea J. Breithaupt, Jr.

Special appreciation is extended to Mr. George Bartholomew, manager of the Flotronics Division, Selas Corporation of America, for providing the ceramic tube bundles used as membrane supports and for his technical assistance.

The cooperation and assistance rendered by the Moss Point Mill maintenance and laboratory staff throughout this project are gratefully acknowledged.

SECTION 1

INTRODUCTION

The highly colored waste waters from integrated pulp and paper mills are the subject of great concern from the standpoints of both control technology and impact on receiving streams. The removal of color from these waste waters is difficult and expensive because the bulk of the color is in the form of soluble organic compounds. A number of color removal processes are available, each with its advantages and disadvantages. Coagulation processes are effective, at the expense of sludge handling problems. Destructive methods, such as ozone oxidation, produce effluents of high BOD content. Adsorption processes, such as activated carbon or resin adsorption, pose the problem of the regeneration of the adsorption media. Conventional biological treatment can be effective in removing low levels of color from some waste; however, biological treatment is inadequate for consistently removing the high levels of color from a pulp and paper mill waste. Reverse osmosis and ultrafiltration are high energy and equipment intensive processes, but they have unique advantages that make them attractive methods for treating pulp mill waste waters.

Reverse osmosis and ultrafiltration have the capacity to selectively remove compounds with different molecular weights and to produce clean permeates for recycle. In a pulp mill, especially a bleached-pulp mill, several waste streams are fairly low in volume and quite high in color concentration, and thus they contribute heavily to the total mill effluent color load. Reverse osmosis and ultrafiltration can be applied successfully to such waste streams. This is accomplished by recycling the high molecular weight compounds which contribute to the color load into the mill recovery system and producing clear permeates for reuse or disposal.

The earlier membrane systems used for this purpose have been limited in application because of the pH and temperature extremes encountered in pulp mill waste waters, the low flux rates obtained, and problems with membrane fouling. Dynamically formed membranes of hydrous metallic oxides have been found to give good results with pulp mill and textile mill waste waters. These membranes can be operated at pH and temperature extremes that would adversely affect conventional membranes while at the same time obtaining much higher flux rates.

This report is the culmination of a pilot plant test project in which dynamic membranes were used to treat pulp mill waste waters *in situ.*

SECTION 2

CONCLUSIONS

The pilot plant operation was erratic because of mechanical problems and design faults. It did not produce enough data for successful scale-up calculations. However, the project did identify several important facets of dynamic membrane reverse osmosis and ultrafiltration treatments of waste waters. The use of dynamic membranes may be a viable alternative to conventional membrane systems. When the units were running well, high fluxes and good rejections of dissolved organics were obtained. However, the high degree of membrane instability demonstrated throughout the pilot plant work revealed a need for further development before dynamic membranes will be commercially acceptable.

In several of the experimental runs, difficulties were encountered in membrane formation because of mechanical problems, which caused poor results in waste water operation. It was demonstrated in subsequent runs that a poor membrane could be improved by a combination of washing techniques and by applying extra layers of membrane. Low fluxes during operation with a good membrane could be raised through appropriate washing procedures.

The ultrafiltration unit membranes could successfully be stored for long periods of time if immersed in water. This indicates that individual modules can be prepared and stored for future use, such as with conventional membrane systems.

SECTION 3

RECOMMENDATIONS

The present regulations on the discharge of highly colored waste waters indicate that color removal processes will be necessary in the future. As pulp mills become more involved with internal recycling, the waste streams will become lower in volume and more concentrated than they are currently. The present high cost of membrane systems may be offset in the future by the need to treat such waste streams. Thus, the development of dynamic membrane systems should continue, especially as these systems are more amenable to pulp mill waste waters than conventional membrane systems.

Specifically, more emphasis should be placed on the mechanical design of the units themselves. Prefiltration of the pulp mill wastes should be performed before membrane treatment to lessen fouling and clogging by pulp fibers. Proper design of the units can make fiber clogging less critical than it was with these pilot units. The future trials should focus on using an inside flow arrangement similar to a shell and tube heat exchanger. Porous stainless steel tubes would allow the use of this configuration at higher pressures than with ceramic tubes. The steel tubes would also allow for welded tube assemblies, and any defective or broken tubes could be plugged in a manner similar to the procedure used on boiler tubes. This would allow a module with individual broken tubes to remain in service. Because the tubes would be supported on the permeate side, no flow restrictions would exist to trap fibers.

Thus, the dynamic membrane system with an extensively prefiltered feed for outside flow modules (carbon, ceramic, or steel tubes), or a slightly prefiltered feed for inside flow, could be developed for pulp mill wastes if care is taken to eliminate the operational problems encountered during this project.

SECTION 4

MEMBRANE DEVELOPMENT

With the advent of stricter limits on effluent quality, increased emphasis has been placed on color removal processes. As a result, a number of processes have been developed, each with its advantages and disadvantages. Lime, alum, or other coagulants remove color effectively, but they generate large volumes of sludge resulting in a disposal problem. Adsorption with activated carbon, synthetic resins, and other adsorbents will also remove color from pulp mill waste waters. However, disposal of the spent carbon or of the regeneration streams complicates the integration of this process into regular mill operations. Biological oxidation in conventional secondary waste treatment systems is not consistently adequate and oxidation with ozone, hydrogen peroxide, or other oxidants is too expensive or otherwise difficult to justify. Other processes, such as solvent extraction, amine precipitation, and electrochemical removal are known but not yet attractive on a commercial scale.

Membrane processes, such as reverse osmosis (also called hyperfiltration) and ultrafiltration, have been applied to many situations in which separation of a solute from a solution is desired (see p. 39 for more detailed description). The processes first became practical in the early 1960's with the development of the first membranes. Since then they have been used to desalinate seawater and brackish groundwaters for potable uses, treat municipal and industrial waste waters, and recycle numerous contaminated process solutions which would otherwise be discarded. In the field of industrial waste water treatment, the potential for application of membrane processes is great because they allow separation of possibly valuable by-products and reuse of clean water. Although the processes are energy intensive, they generate no sludges and do not consume a large amount of chemicals.

MEMBRANE CHARACTERISTICS

The growing interest in reverse osmosis and ultrafiltration for desalination and waste water treatment has generated the need for improved membranes. Thus, over the past decade a number of membrane materials have been used in attempts to overcome the shortcomings of the original cellulose acetate membranes. The different types can be subdivided into two groups: precast and dynamic membranes.

Precast Membranes

The use of reverse osmosis and ultrafiltration for commercial scale applications became possible with the development of cast cellulose acetate film as a membrane material. Although other membranes have been developed in attempts to improve performance, cellulose acetate is still widely used (6, 9, 19, 21, 23, 24, 29, 30, 31, 32). It can be cast in the form of flat sheet, spiral-wound, or tubular modules. It is limited in that pH and temperature must be limited to ranges of 3-8 and up to 35-38°C, respectively. At pH values outside this range the ester groups hydrolyze, and the membrane structure deteriorates at higher temperatures. The membrane gives flux rates of 0.6 to 0.8 $m^3/m^2/d$ (15 to 20 gfd) at ultrafiltration pressures of $2.5x10^5$ to $1x10^6$ Pa (35 to 150 psi) and flux rates of about 0.3 $m^3/m^2 d$ (7 gfd) at reverse osmosis pressures of $2x10^6$ to $4x10^6$ Pa (300 to 600 psi). At these conditions, cellulose acetate will reject molecules of molecular weights of 10,000 or higher when operating in the ultrafiltration mode and molecules of molecular weight of 80 or higher when operating as a reverse osmosis unit.

To improve flux rates and increase removals, various modifications to the basic cellulose acetate structure have been tried. Cellulose acetate is a very polar molecule which accounts for the passage of water and polar molecules through the membrane. Cellulose acetate butyrate (CAB) and cellulose acetate triacetate (CA3) were developed by substituting butyl and acetyl groups, respectively, for free hydroxide groups in the basic cellulose acetate structure (8). The rejections improved, somewhat, at the expense of lower fluxes. Other modifications, such as cellulose acetate O-propyl sulfonic acid (CAOPSA) and cellulose acetate (E398-10), have also been used, with little or no improvement over the original structure (25).

The aromatic polyamide membranes, developed by Du Pont, are generally formed into hollow fiber modules (9, 21, 29, 31). The polyamide material can be operated in a pH range of 4-11 at temperatures up to 38°C. It gives similar removals and fluxes as cellulose acetate and thus is useful when pH values higher than 8 are encountered. One drawback is that the membrane deteriorates in the presence of chlorine, which precludes its use as a cleaning agent. The NS-type membranes, made of polyethylenimine crosslinked with tolylene 2,4- diisocyanate, were developed by the North Star Research Company (9, 12, 25, 31). This material is essentially nonpolar and is usually cast in tubular modules. The NS membranes (NS-1, NS-100, and NS-200) give better removals of polar organics than cellulose acetate, and they have been used successfully at very low and high pH values (0.5, 12 respectively) (25). The flux rates are quite similar to those obtained with cellulose acetate membranes.

Polysulfone membranes have the advantage of operating at higher temperatures (up to 88°C) and wider pH ranges (1-13) (14, 23, 28, 32, 33). Solute removals are slightly lower than those usually obtained with cellulose acetate, but the membrane can be used to treat effluents which could not be treated with cellulose acetate. Fluxes are higher than those obtained with cellulose acetate but drop rapidly as the total dissolved solids concentration increases. Polysulfone membranes are usually cast in tubular form and are sometimes used as a support for other membranes.

Several other membrane materials have been used for reverse osmosis and ultrafiltration, but they have not gained as widespread application as those mentioned above. Union Carbide Corporation developed an ultrafiltration unit using a proprietary inorganic membrane (UCARSEP^R) which can be used in pH ranges of 1-14 and temperatures up to 130°C, cast on a tubular carbon support (22, 32). Membranes cast of poly 2,2 (m-phenylene)-5,5 bibenzimidazole and sulfonated polyphenylene oxide have been developed, but they gave much lower removals of salts and organics than cellulose acetate, polyamide, and NS-type membranes (31). A membrane formed from poly (ether/amide) deposited on a polysulfone spiral-wound module obtained 99+% removal of salt and fluxes slightly better than cellulose acetate membranes at $6.9x10^6$ Pa (1000 psi). This membrane can be used in a pH range of 3-12 and temperatures up to 55°C, and it resists chemical attack, making cleaning easier than with other membranes (34). Another new membrane was developed by coating a polysulfone hollow fiber with a furan resin and crosslinking it with sulfuric acid (35). The membrane gives excellent salt rejection (99+%) at pressures of $5.5x10^6$ Pa (800 psi) and can operate in pH ranges of 1.5 to 13. The flux rate obtained is low, in the order of 0.08 to 0.12 $m^3/m^2/d$ (2-3 gfd), but productivity can be high in a hollow fiber module because thousands of fibers can be used in a single module.

A number of membranes have been developed for reverse osmosis and ultrafiltration which can be used in various configurations and in more extreme conditions than cellulose acetate. However, the flux rates and solute rejections have not improved dramatically with the precast membranes. Fouling problems have been lessened but not eliminated. It is anticipated that more effort will be expanded in the future in an attempt to produce better membranes.

Dynamic Membranes

In addition to the developmental work being done with precast membranes, it was found that membranes could be formed dynamically by circulating a suspension of a suitable substance over a porous support under pressure. The substance coats the porous support to form a membrane layer with a porosity less than that of the support material. Such a membrane is called a dynamically formed, or dynamic, membrane. The first feasible dynamic membranes were formed at the Oak Ridge National Laboratory in the mid–1960's. In 1966 it was reported that a membrane made of hydrous thorium oxide had been developed (35). It was found that other metals, capable of forming hydrous oxides, such as Fe(III), Zr(IV), Bi(III), and Sn(IV), could also form dynamic membranes. Studies in later years showed that dynamic membranes could also be formed from natural polyelectrolytes such as humic acid (37) and constituents usually found in pulp and paper mill effluents (38, 39, 40).

The metal oxide which has received the most attention is hydrous zirconium (Zr[IV]) oxide because of its ion exchange capabilities. The fluxes obtained were high, even with thick membranes, and it was discovered that a dynamic membrane gave better flux rates than a precast membrane of the same material. It was also found that the dynamic Zr(IV) oxide membranes had a self-rejecting property, in that after a certain thickness had formed, the membrane material would begin to reject further formation. The dynamic membranes were first applied to desalination of seawater and brackish waters, but it was found that they would reject organic solutes as well as salts. In tests with spent sulfite liquors, it was found that a Zr(IV) oxide dynamic membrane formed before application of the liquor gave better removals than membranes formed with the liquor alone, or a mixture of the liquor and zirconium (36). A separate study showed that dynamic membranes could be formed from calcium based spent sulfite liquor, but performance was very erratic. The optimum performance obtained 90% rejection of color at flux rates of 1.2 $m^3/m^2/d$ (gfd) at 3.5×10^6 Pa (500 psi) (39).

In 1969, a dual layer membrane consisting of an underlayer of hydrous Zr(IV) oxide and an overlayer of poly acrylic acid (PAA) was found to have ion exchange characteristics which indicated a number of possible applications. The first membranes were formed on porous carbon tubes manufactured for use as electrodes, but in later work other porous supports, such as ceramic and stainless steel tubes and polymeric materials, were successfully used. It was found that the best pore diameter was approximately 0.25 μm, and that a precoating of a filteraid would be necessary for supports with pore diameters greater than 10 μm. Concentration polarization was found to be more important with dynamic membranes than with precast types, so it was initially believed that high circulation velocities (greater than 6.1 m/sec [20 ft/sec]) would be needed to obtain good flux rates and rejections. High pressures were found to be necessary for good rejections with the Zr(IV) – PAA membranes. Tests with salt solution showed that, at a pressure of 6.6×10^5 Pa(95 psi), a flux rate of 27.1 $m^3/m^2/d$ (666 gfd) and 19% rejection were obtained, while at a pressure of 6.6×10^6 Pa (950 psi) the flux dropped to 6 $m^3/m^2/d$ (147 gfd) with a 94% rejection (36). This lowered flux rate was still much higher than those being currently obtained with precast membranes.

Tests using Zr(IV) – PAA membranes to treat textile wastes were reported in 1973 (41). At a pressure of 6.9×10^6 Pa (1000 psi) and a temperature of 60°C, 99% rejection of color was obtained at flux rates of 1.6 – 3.2 $m^3/m^2/d$ (40 to 80 gfd). The tests showed that high velocities did indeed alleviate fouling and also that higher operating temperatures resulted in higher fluxes. Four different porous supports were used: ceramic tubes (0.27 μm pore diameter) manufactured by Selas Corporation of America–Flotronics Division, Union Carbide carbon tubes (563-6C), and two steel tubes wrapped with polymeric sheets (Millipore, 0.22 μm pore diameter, and Acropor AN, 0.45 μm pore diameter). Further tests were also being performed using lignins to form a dynamic membrane on a cellulose acetate membrane that had deteriorated (38). The results indicated that a dynamic membrane formed from pure lignin and/or pulp and paper mill effluents could "tighten" an old membrane or close up small defects in a leaking module. This lignin membrane was not dislodged under high velocity flow conditions but was easily removed by regular cleaning techniques, such as detergent washes. However, the membrane had to be formed at a pH of 4 to be effective and would only last for 3 or 4 days.

The Office of Saline Water contracted with Oak Ridge National Laboratory to build a pilot plant for the purpose of studying dynamic membrane desalination. The tubular supports available were nearly equal in quality, so ceramic tubes manufactured by the Ferro Corporation were arbitrarily chosen. These tubes required precoating with diatomaceous earth before membrane formation because the pore diameters were approximately 10μm. The flow velocity was studied, and it was found that reducing the velocity from the usual 9.1 m/sec (30 ft/sec) down to 3 m/sec (10 ft/sec) did not significantly affect the flux rate. The percent rejection was reduced slightly, but the pressure drop across the test module was reduced from 3.2×10^5 Pa (47 psi) to 4.4×10^4 (6.4 psi), respectively, allowing significant savings in pumping costs. The formation of the zirconium layer was formed from an initial value of 200 $m^3/m^2/d$ (5000 gfd) down to 40.7 $m^3/m^2/d$ (1000 gfd). If the zirconium layer were allowed to build up further, the final flux after the poly acrylic acid layer formation would be too low to be practical. The performance of the membrane was found to be adversely affected by hard water, and pretreatment to soften the water was necessary. In actual pilot plant tests, it was found that reducing the flow velocity from 7.1 m/sec (30 ft/sec) to 4.6 m/sec (15 ft/sec) resulted in a slight decrease in percent rejection because of concentration polarization. However, the pressure drop across the sixteen tubular modules (mounted in series) decreased, and the flux actually improved in the last few bundles (36).

Dynamic membranes for reverse osmosis and ultrafiltration were also being tested for treating pulp and paper mill effluents in the cooperative efforts between Oak Ridge National Laboratory and International Paper Company (40). Using several membrane supports, the following tests were performed: (1) reverse osmosis treatment of simulated screen room effluents and caustic bleach plant waste water using Zr-PAA membranes and (2) ultrafiltration treatment of the caustic bleach plant waste water with zirconium and polyvinylpyrrolidine membranes. The Zr-PAA membrane, operated at 6.9×10^6 Pa (1000 psi), gave 99+% color and 95-98% organic carbon rejections at flux rates of 1.3 to 3.9 $m^3/m^2/d$ (31 to 96 gfd), while treating the screen room effluent. Treatment of the bleach plant effluents gave similar removals, but the concentrated feed had so much chloride in it that it would be impractical to introduce it into the mill recovery system. The ultrafiltration unit (single layer zirconium membrane) gave 99% color and about 90% total organic carbon removals at operating pressures of 1.4×10^6 Pa (200 psi). When the pressure was raised to 6.9×10^6 Pa (1000 psi), the chloride rejection and resulting chloride concentration in the concentrated feed was too high, as with the reverse osmosis unit. Similar results were obtained with the poly(vinyl pyrrolidine).

Later work with kraft mill wastes involved testing of a number of membrane materials, using bleach plant waste waters (42). The original Zr-PAA membrane was the best choice for reverse osmosis applications; whereas the poly(vinyl pyrrolidine) was the favorite for the ultrafiltration. However, for ultrafiltration, three other membranes also looked promising: the Zr single layer membrane; a polymer called pluronic 98 (80% poly[oxyethylene], 20% poly[oxypropylene]) manufactured by Wyandotte Chemicals Co.; and a dual layer of hydrous zirconium and silicon oxides. An investigation involving textile dyeing waste waters compared dynamic Zr-PAA membranes with precast cellulose acetate and aromatic polyamide (26). The dynamic membrane gave equal removals, while operating at higher temperatures and wider pH range feeds with no prefiltration. The dynamic membrane also obtained higher flux rates and allowed higher productivity.

Dynamically formed membranes have been shown to be capable of producing high flux rates and rejections of various solutes. Presently, they are not used as widely as the precast types, simply because they were developed later. However, the engineering aspects of the design of waste water treatment systems for industrial effluents, such as temperature, pH, pretreatment needs, and reliability, make dynamic membrane systems quite attractive. As others have recognized, in the design of membrane systems to remove high molecular weight compounds, the choice of engineering is more important than the choice of the membrane (8).

SECTION 5

EXPERIMENTAL

LABORATORY STUDIES

Studies performed at Oak Ridge National Laboratory have established that dynamic membrane reverse osmosis and ultrafiltration are capable of removing color from pulp and paper effluents (40, 41). Additional laboratory studies on operating parameters were necessary to obtain data for pilot plant work.

Reverse Osmosis

An extended study with a 19-tube (ceramic) bundle in a flow scheme as shown in Figure 1 was performed and is summarized in Figure 2. The bundle had been used previously for textile dye wastes at temperatures up to 94°C and was cleaned by immersion in a chromic acid solution before formation of a hydrous Zr(IV) oxide-polyacrylate membrane. The membrane gave a salt rejection of 94% and a flux rate of 3.1 $m^3/m^2/d$ (75 gfd) at the end of membrane formation. The waste water fed to the module was a simulated decker filtrate produced by diluting weak black liquor (nominally 12-15% total solids) to a concentration of about 1% total solids. The flux dropped to about 1.6 $m^3/m^2/d$ (40 gfd) in approximately 1 week, at which time the unit was washed with a 0.1M $Na_2CO_3 - NaHCO_3$ solution (pH ≈3) which restored performance. A second wash at about 250 hours was less successful, and a subsequent wash was performed at a lower pressure, in the hope that the lower flux would make the wash more effective. Another wash sequence at about 340 hours included washes with 0.1 M HNO_3 and 0.1 M H_2SO_4, but they had little benefit. The bundle was washed with acid and base, and the membrane reformed, but the flux deteriorated rapidly and improved only slightly after a 0.1 M H_2SO_4 wash. The bundle was removed, soaked in chromic acid to remove the previous membranes, and a new membrane formed. The flux rate dropped to 1.2 from 1.6 $m^3/m^2/d$ (30 to 40 gfd) and stabilized at about 1.2 $m^3/m^2/d$, maintaining this level for the duration of the run.

In an attempt to determine whether a change in the pore dimensions on the surface accounted for the deteriorating properties seen in Figure 2, the tube bundle was cleaned again and pretreated with a filteraid before the next membrane formation. The pretreatment did not cause a definite improvement, as seen in Figure 3. The inadvertent shutdowns prevented a clear conclusion, because membranes formed on filteraid layers tend to be unstable if operating interruptions occur.

Ultrafiltration tests have indicated that the presence of silicate helps to slow flux decline. This same bundle was tested with hydrous Si(IV) oxide present in several different patterns during membrane formation. The results are shown in Figure 4 (one run was with a single tube rather than a bundle). However, little if any improvement was obtained in cases where Si(IV) was present during the membrane formation.

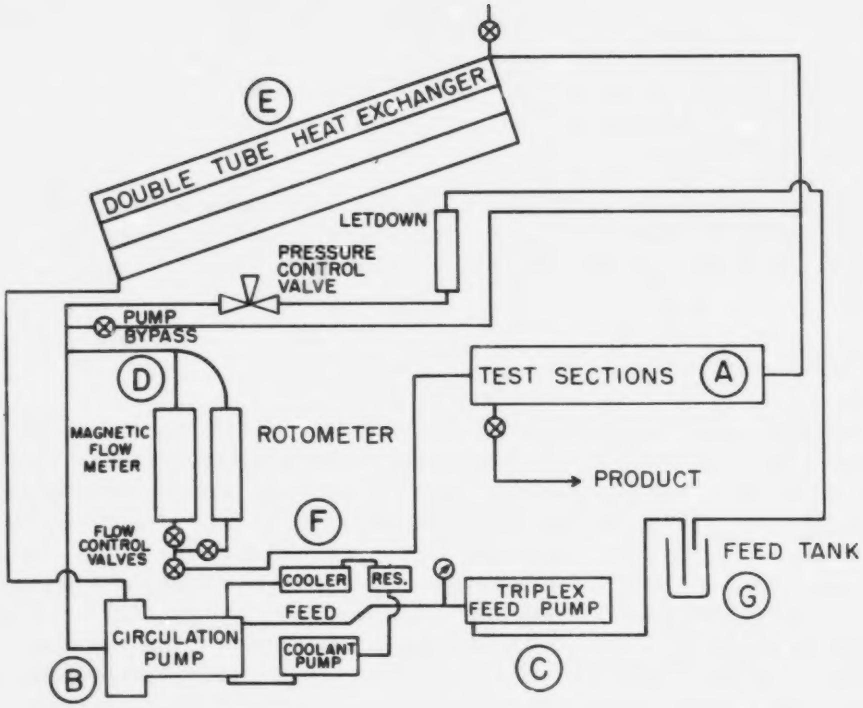
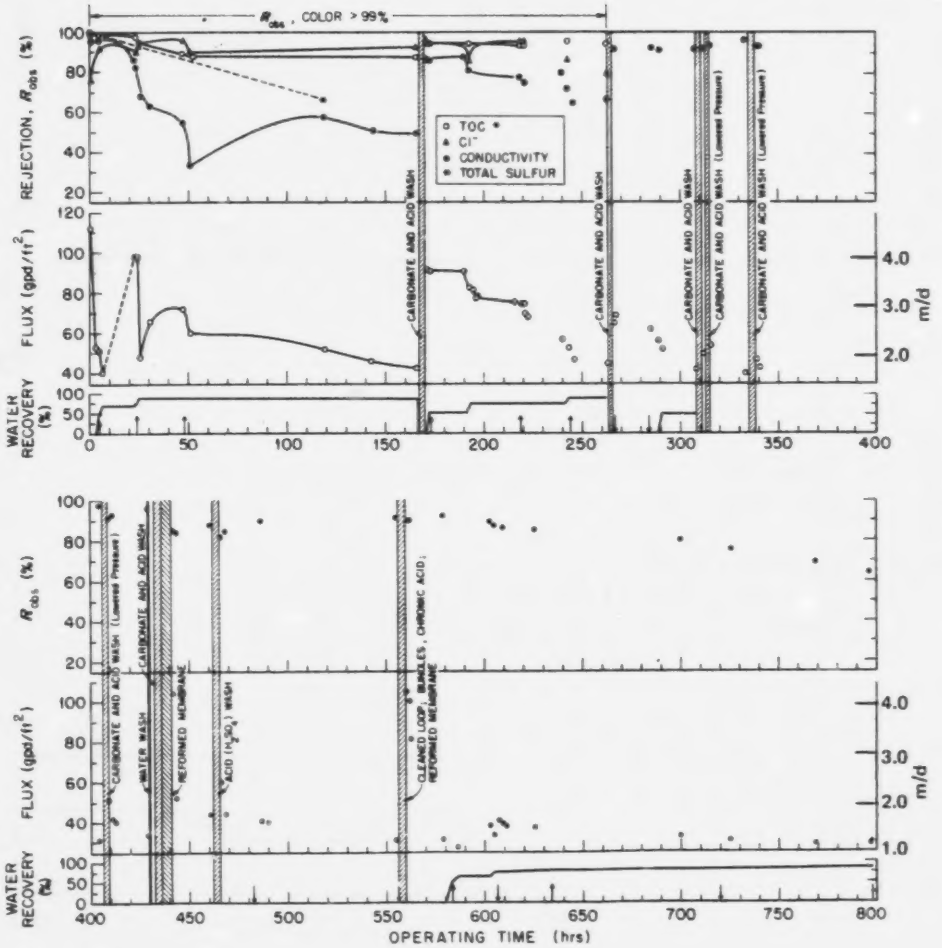


Figure 1. Flow diagram of high-circulation-velocity hyperfiltration loop.



*Total organic carbon

↓ Shutdown ; ↑ Fresh Diluted Weak Black Liquor Introduced

Figure 2. Hyperfiltration of simulated pulp-washing effluents: washing and regeneration tests.
(950 psi; 15 ft/sec; 55°C; pH 7-9)
(6.55×10^6 Pa; 4.6 m/sec)

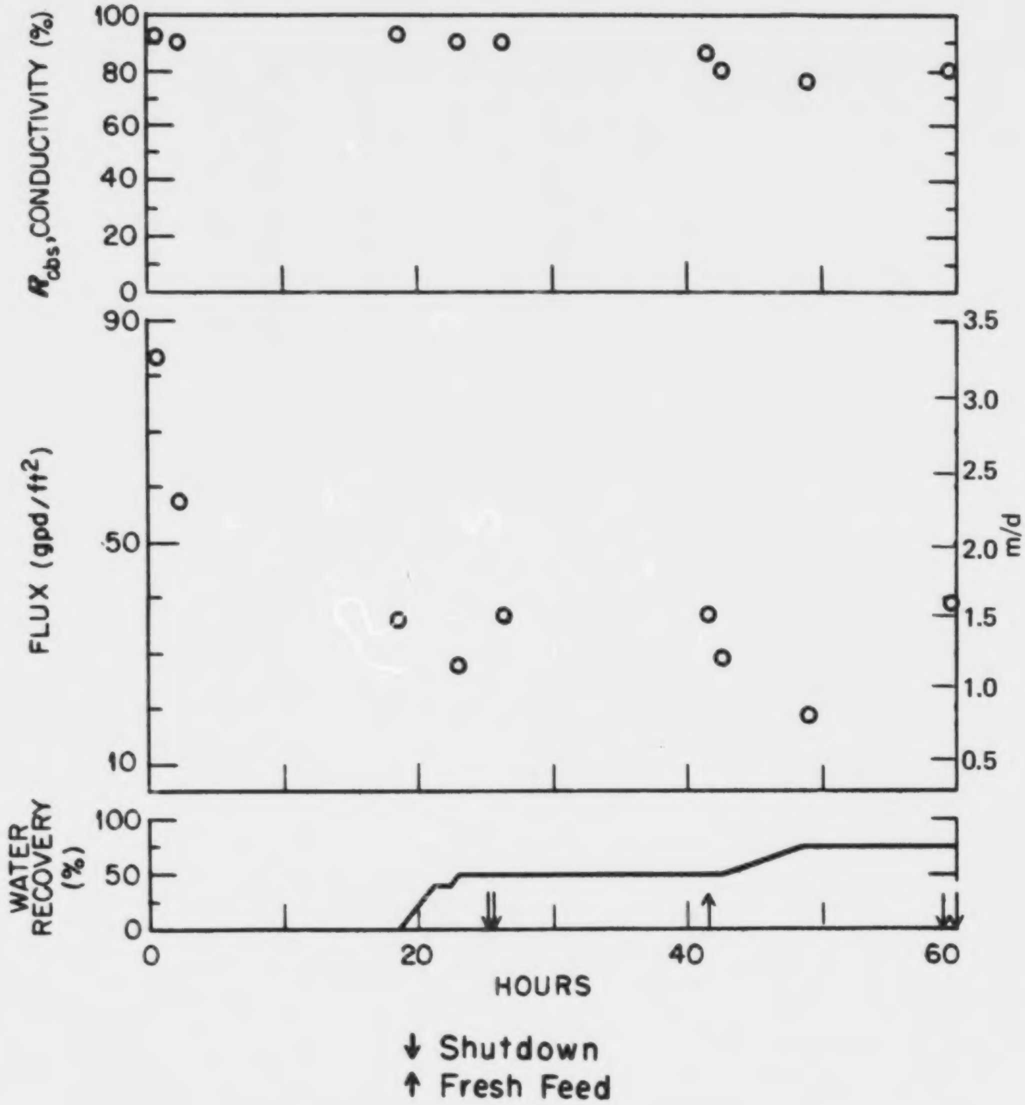


Figure 3. Effect of filteraid pretreatment of used 19-tube 0.27μ Selas ceramic bundle.

(950 psi ; 15 ft/sec ; 55°C ; pH 7.3-8.6)
(6.55×10^6 Pa ; 4.6 m/sec)

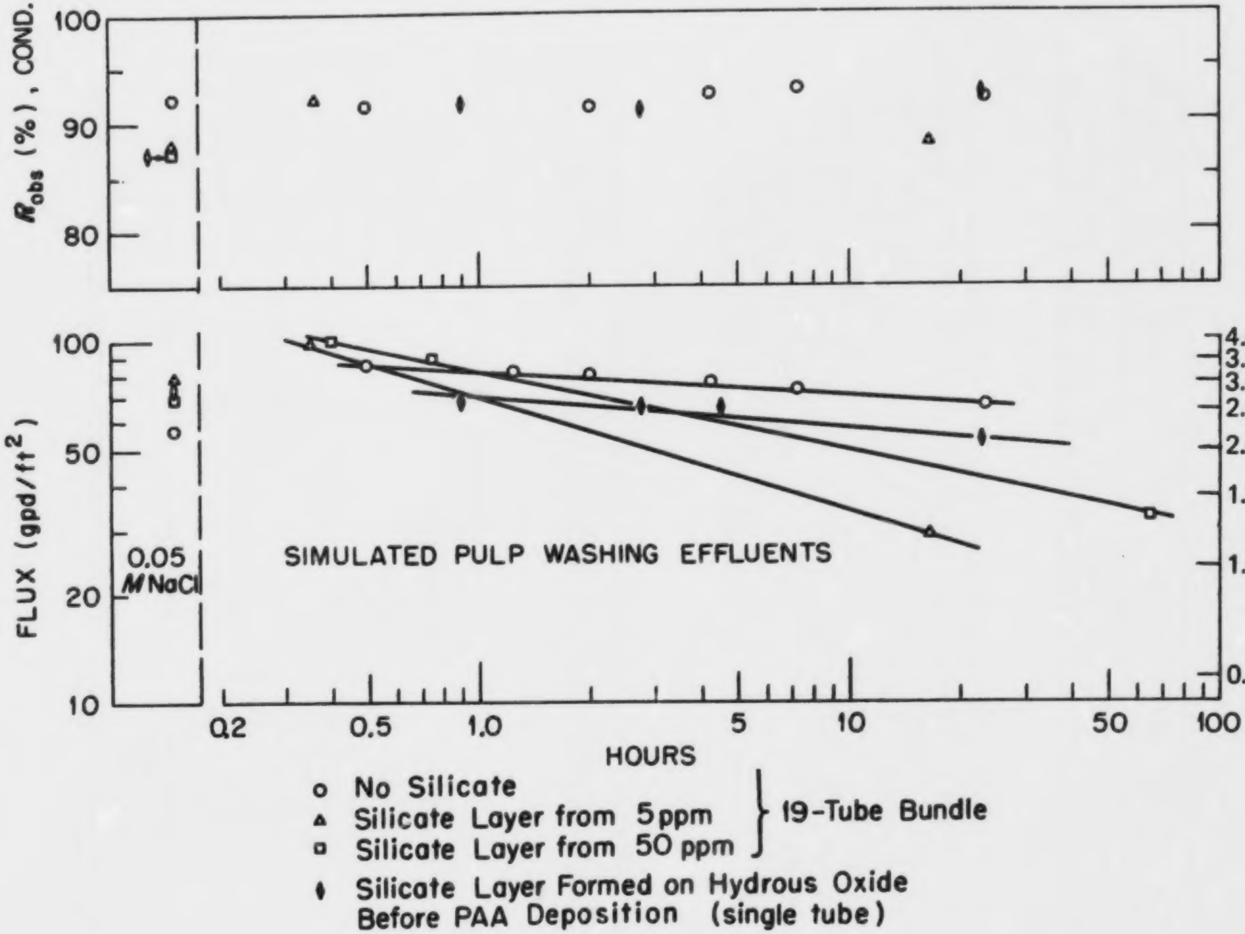


Figure 4. Effect of silicate on hyperfiltration by hydrous ZR(IV) oxide-polyacrylate membranes on 0.27μ Selas ceramic tubes.

(950 psi; 15 ft/sec; 55°C; Feed: Weak Black Liquor Diluted to 1% Solids, pH 7 to 8.3)
(6.55×10^6 Pa; 4.6 m/sec)

Other membrane supports were tested in addition to the porous ceramic tubes. Tubes made of porous 316L stainless steel were provided by the Mott Metallurgical Corporation (Farmington, Connecticut). All but one were 6.35×10^{-3} m (0.25 in) outside diameter with a thin layer of fine pores on the outside. The listed manufacturer's pore size refers not to actual pore diameter but to the particle size removed when operated with a cross flow of feed past the surface. As seen in Table 1, the nominal pore sizes tested were 0.2 and 5 μm, however, the manufacturer's literature suggests that the actual pore sizes may be as much as a factor of 10 greater than the nominal size. The optimum pore size appears to be in the range of 0.1 to 0.5 μm, and earlier work indicates that filteraid pretreatment is desirable for pore sizes greater than 1 μm. As seen in Table 1, the membrane properties after formation confirm that these Mott tubes have pore sizes too large for use without filteraid.

The membranes formed after a filteraid pretreatment gave operating properties within the customary ranges. The filteraid pretreatments used in Runs 10—CI and 10—CJ were fine diatomite (Johns-Manville Celite 505) followed by an even finer carbon black (Cabot Corporation Regal SR). Carbon black alone was used in Run 7—NM and was fed with the zirconyl chloride. The membranes from Runs 10—CI and 7—NM were tested with the simulated decker filtrate (weak black liquor diluted to about 1% total solids and neutralized). Initial rejection and fluxes were in the normal ranges, but the membrane in Run 10—CI deteriorated dramatically overnight, producing a black filtrate the next morning. The tube was backwashed, and the membrane for Run 10—CJ formed. In Run 7—NM, the performances of both the Mott and Selas tubes were stable overnight (Fig. 5).

TABLE 1. SUMMARY OF TESTS OF MOTT POROUS STAINLESS STEEL FILTERS
~ 15 ft/sec; 25-30°C; 950 psig; pH ~ 4 (hydrous ZR (IV) oxide), 6.5-7 (PAA)

Run No.	Support, Mfgs. Designation (I) Inside (O) Outside	Filteraid	Membrane				Feed
			Hyd. Zr(IV) Oxide		With PAA Layer		
			gpd/ft^2	R_{obs}, %	gpd/ft^2	R_{obs}, %	
10-CG	5 μ(I)	None	210	25	34	66	0.05 M $NaNO_3$
10-CH	5 μ(I)	None (boiled Zr(IV))	310	26	90	23	0.05 M $NaNO_3$
10-CI	5 μ(I)	25 ppm Celite 505 25 ppm Regal SR	300	46	100	90	0.05 M $NaNO_3$
10-CJ	5 μ(I)	25 ppm Celite 505 25 ppm Regal SR	320	40	40	93	0.05 M $NaCl_3$
7-NK	0.2 μ(I)	None	135	35	14	64	0.05 M NaCl
7-NL	0.2 μ(O)*	None	685	44	84	63	0.05 M $NaNO_3$
7-NM	0.2 μ(I)	25 ppm Regal SR (pre-mixed with zirconyl chloride)	270	19	50	95	0.05 M $NaNO_3$

*10 micron tube, with 0.2 μ rated coating on outside.

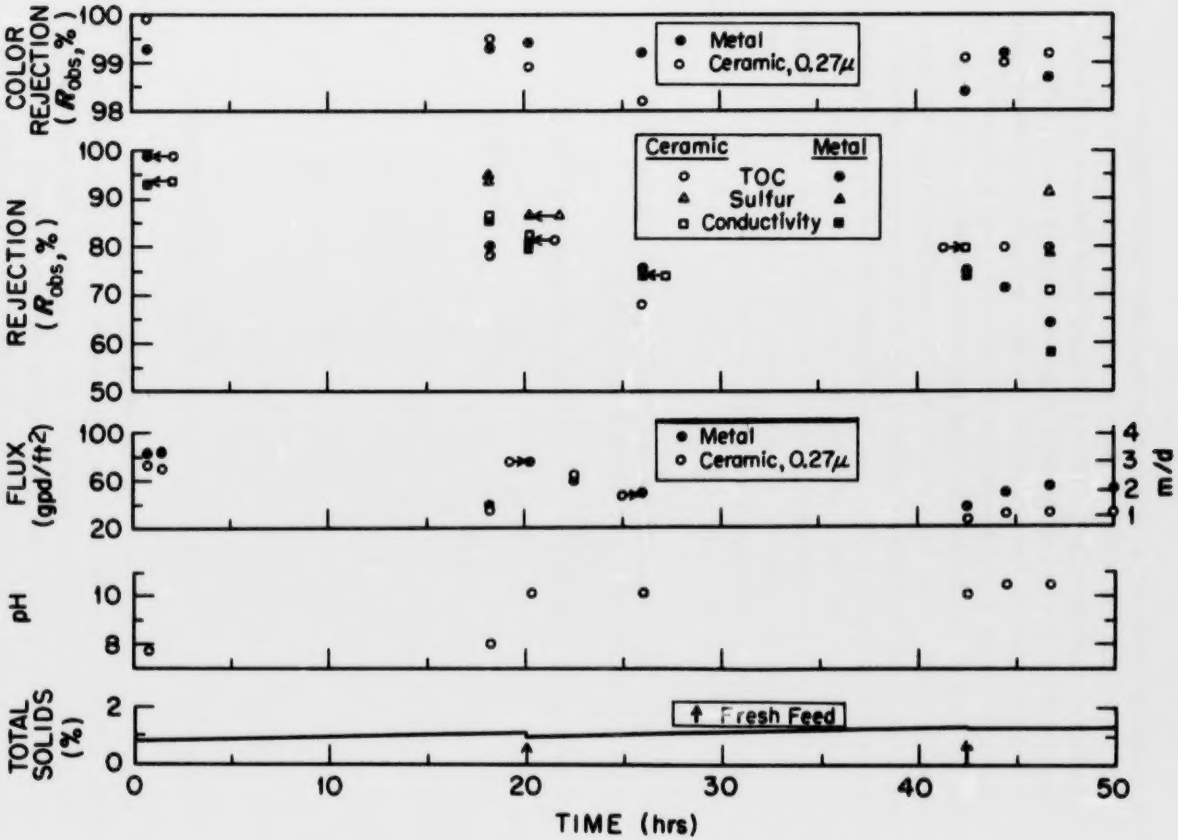


Figure 5. Comparison of hyperfiltration of simulated pulp-wash liquor: ceramic and filteraid-treated porous metal supports.

950 psi 15 ft/sec 55°C
6.55×10^6 Pa 4.6 m/sec

However, the next morning fresh unneutralized feed was introduced and the rejection from both tubes fell, precluding a direct comparison with past experience. The conductivity rejection for the Selas tube was 72% at a flux of 1.30 $m^3/m^2/d$ (32 gfd) after 1 day, while that for the Mott tube was 58% at a flux of 2.24 $m^3/m^2/d$ (55 gfd). The total sulfur rejections were 91% for the Selas and 79% for the Mott tubes. At the time of this test, stainless steel tubes with pore sizes in the 0.5 μm range were not available, and the use of a filteraid was necessary.

After the stainless steel tubes were removed, a ceramic tube manufactured by Raypak (now Rev-O-Pak, Inc., Newbury Park, California) was installed. The tube was mounted in an outside flow configuration. A filteraid pretreatment (25 ppm Celite 505 and 50 ppm Regal SR) was used prior to membrane formation. The membrane deteriorated because of an unscheduled test loop shutdown, and a second acidic PAA layer formation was performed. As seen in Table 2, the membrane properties were close to the expected range. The 0.45 μm pore size Acropor control membrane support gave 92% salt rejection at 3.63 $m^3/m^2/d$ (89 gfd) using a circulation velocity of 9.1 m/s (30 ft/sec) as opposed to 4.6 m/s (15 ft/sec) with the Raypak tube. This membrane was used as a control to check general system operation. Neutralized simulated decker filtrate was introduced, and conductivity rejection was good although the initial flux decline was high. After a day of operation, weak black liquor was added to bring the total solids content up to 8%. The flux and rejection declined immediately and the clear, colorless permeates became turbid and yellow. At the end of the run a tube inspection revealed that part of the black precoat had been lost. The Acropor support also showed unusual deterioration, indicating that some upset had occurred. Its conductivity rejection was 59% at a flux of 1.92 $m^3/m^2/d$ (47 gfd).

TABLE 2. HYDROUS Zr(IV) OXIDE-POLYACRYLATE MEMBRANE ON RAYPAK CERAMIC TUBE, PRETREATED WITH FILTERAID
(15 ft/sec)

Time Hrs.	pH	Temperature °C	Flux gpd/ft^2	R_{obs}, % Conductivity
	After membrane formation (0.05 M NaCl)			
	6.6	25	74	94
0	Introduced diluted weak black liquor, 1% solids			
1	7.3	53	76	94
3	–	55	56	94
6	7.5	55	49	94
23	8	55	46	95
24	Introduced diluted weak black liquor, 8% solids			
27	7	55	10	72
47	8.2	35	63	57

In the above results, as well as in past work with pulping effluents, neutralization of the feed has been considered necessary. This was done because the polyacrylate layer of the membrane tends to be displaced at pH values above 10 (rapidly above pH 11). A lower pH was also thought to be necessary for the rejection of the low molecular weight sulfur containing compounds (for chemical recovery). However, the necessity for feed neutralization has been re-examined in the light of several factors. It has been noted that the reaction of some feed constituents with the sulfuric acid used for pH adjustment produces species which adversely affect membrane performance. Fouling of the membrane may also be less rapid at higher pH levels. Although rejection of

NaCl by hydrous Zr(IV) oxide membranes is low in its cation-exchange mode at high pH, Na_2SO_4 is appreciably filtered because of its divalent co-ion. Thus, permeates can be recycled into the earlier stages of pulp washing and the sulfur compounds will eventually arrive in the chemical recovery system. Selas Corporation has modified their ceramic tubes to be more resistant to hot alkaline solutions, and tube damage from high temperature operation has been minimized. It is possible that a dynamic membrane formed from feed constituents over the preformed layer may have a useful rejection capacity. Thus, if the polyacrylate was degraded at the higher pH of the unneutralized feeds, adequate performance may still occur. All of these observations indicated that pH adjustment was unnecessary, and thus subsequent testing was done with unneutralized feeds.

A run in which three membranes were simultaneously tested is summarized in Figure 6. The three membranes were (1) a Kelzan (xanthan gum) membrane on a single Selas ceramic tube, (2) a hydrous Zr(IV) oxide-polyacrylate membrane (Zr(IV)-PAA) mounted on a Selas 19-tube bundle, which had been severely fouled in a previous test, and (3) a hydrous Zr(IV)—Si(IV) oxide membrane, also on a Selas 19-tube bundle that had been previously used in ultrafiltration tests with bleach plant and other wastes. The Zr(IV)—PAA membrane gave fluxes of only 0.81 to 1.22 m^3/m^2/d (20 to 30 gfd) in the previous test, but there was no significant deterioration in flux, even though solids concentrations comparable with the level of weak black liquor were attained. The feed in this test was the diluted weak black liquor, but without any acid addition for pH adjustment. The unusual number of shutdowns indicated in Figure 6 were the result of tube failures mostly in the Zr(IV)—Si(IV) oxide bundle which was constructed of thin-walled tubes and had an extensive history of long operating periods at low pressure. This bundle was demolished after about 40 hours in this run. The rejections for all parameters were higher for the Zr(IV)—PAA membrane than for the others. The most notable aspect was the relatively high total sulfur rejection by this membrane at high water recovery (84%) when the concentration of weak black liquor (about 12% total solids) was reached. At this point, the permeate contained 2300 ppm total organic carbon (TOC), 500 ppm total sulfur, and 360 units of color, while the concentrated liquor contained 34,500 ppm TOC, 3400 ppm total sulfur, and 236,000 units of color.

The test results indicated in Figure 7 are for a newly formed hydrous Zr(IV) oxide-polyacrylate membrane (88% salt rejection and flux of 4.07 m^3/m^2/d [100 gfd] at 25°C). The fluxes for this membrane, which was formed on a new Selas 19-tube bundle, were substantially higher than those for the fouled membrane in Figure 6. The rejections obtained were similar.

The next investigation was a direct comparison of the stainless steel tubes with the ceramic tubes. The pore sizes of the stainless steel tubes were too large and an application of filteraid was necessary to form a thin layer of suitable pore size. The history of the five membranes is summarized below, along with the symbols used to represent the results in Figure 8.

☐ A Mott tube with nominal pore size of 0.2 μm (which could be 10 times larger) was used as the support for a Zr(IV)—PAA membrane using Cabot Regal SR carbon black as a filteraid. The rejection was 94% at a flux of 2.44 m^3/m^2/d (60 gfd) for 0.05 M $NaNO_3$.

◊ A Mott tube with a nominal pore size of 5 μm was used as the support for a Zr(IV) — PAA membrane with no filteraid, although some residual carbon from previous runs was noticed. The rejction was 94% at a flux of 2.04 m^3/m^2/d (50 gfd) for 0.05 M $NaNO_3$.

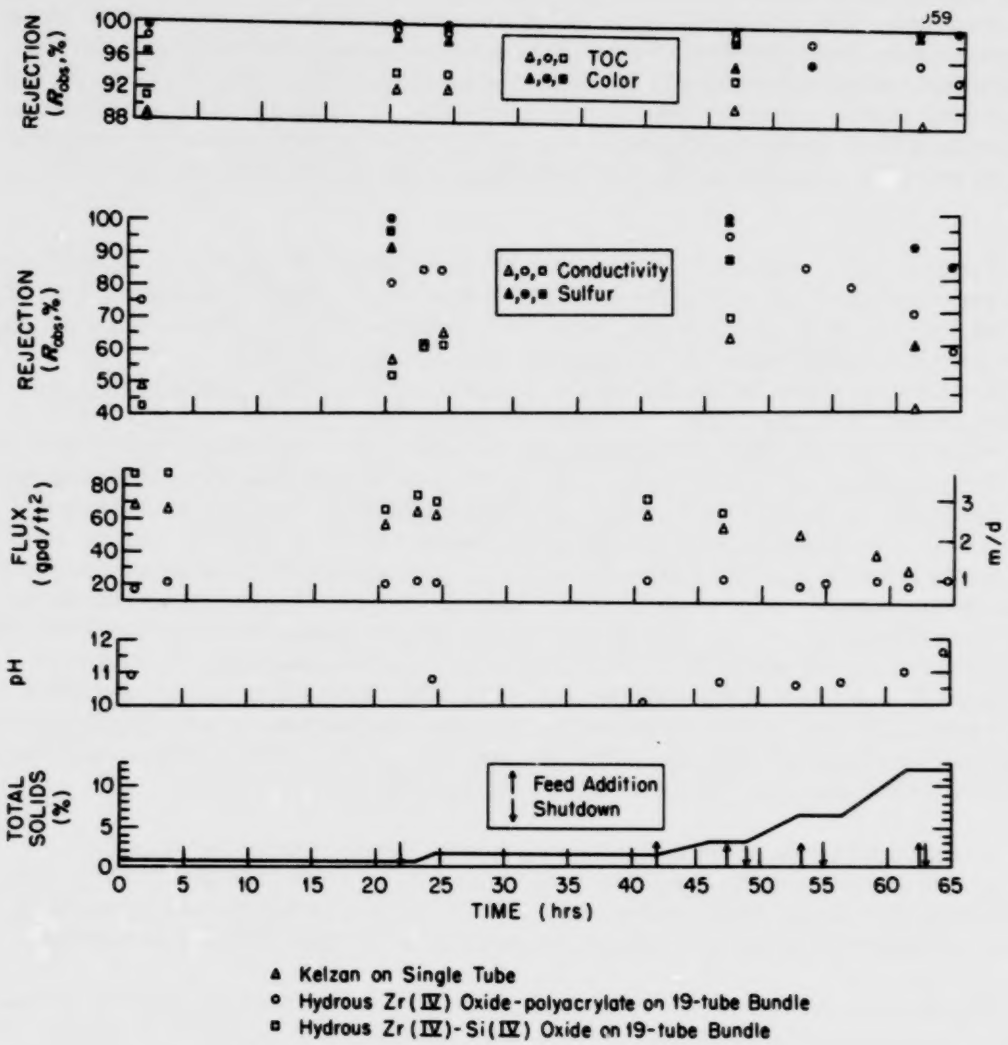


Figure 6. Hyperfiltration of simulated unneutralized pulp-wash liquors with various membranes.

950 psi 15 ft/sec 55°C 0.27μ Selas Ceramic
6.55×10^6 Pa 4.6 m/sec

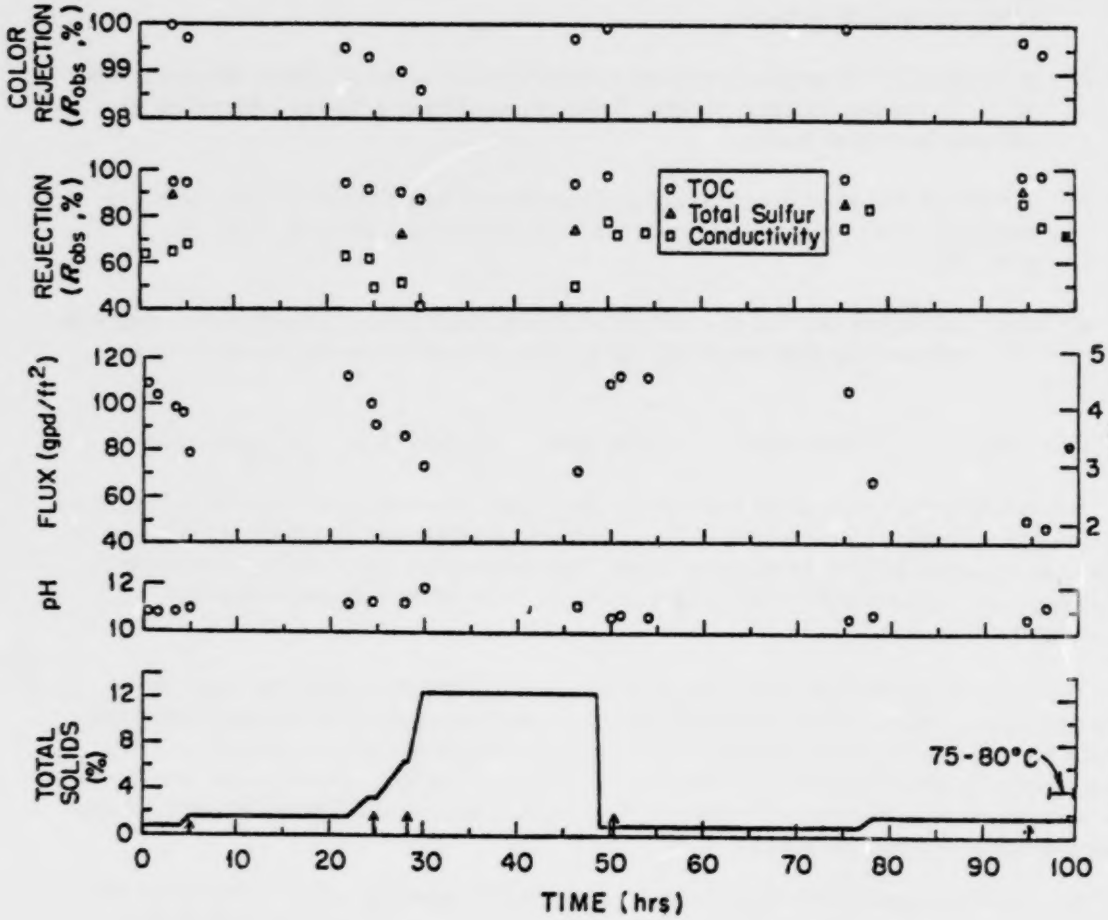


Figure 7. Hyperfiltration of unneutralized simulated kraft-wash liquors.

950 psi	15 ft/sec	55°C	↑ Fresh Feed
6.55×10^6 Pa	4.6 m/sec		

○ A hydrous Zr(IV) oxide membrane was formed on a Selas 19-tube ceramic (0.27 μm average pore size) bundle. At pH 4, rejection was 40% at a flux of 10.4 $m^3/m^2/d$ (255 gfd) for 0.05 M $NaNO_3$.

△ A hydrous Zr(IV) oxide-polyacrylate membrane was formed on a Selas 19-tube ceramic (0.27 μm average pore size) bundle. Rejection was 85% at a flux of 3.46 $m^3/m^2/d$ (85 gfd) for 0.05 M $NaNO_3$.

▽ A hydrous Zr(IV) oxide membrane was formed on a Selas 19-tube ceramic (0.27 μm average pore size) bundle and exposed to a polyacrylic acid solution at pH 2 for 5 minutes.

All were installed in a loop for tests with diluted weak black liquor, but preliminary tests with 0.05 M $NaNO_3$ indicated considerable deterioration, as the results below indicate (% R, flux in $m^3/m^2/d$):

□ (34%, 285)   ◊ (67%, 125)   ○ (10%, 385)   △ (64%, 115)   ▽ (63%, 190)

The two hydrous Zr(IV) oxide modules (○ and ▽) were removed, and the others subjected to an acid cycle containing polyacrylic acid. The rejections were restored, but there was evidence of membrane instability on the stainless steel tubes. The two hydrous Zr(IV) oxide bundles were reinstalled, and unneutralized diluted weak black liquor trials performed with the results summarized in Figure 8.

The initial fluxes through the Mott steel tubes were high and their permeates were highly colored. However, the fluxes decreased and rejections improved, apparently because of plugging of tube imperfections by feed constituents. During the overnight operation, the hydrous Zr(IV) oxide module failed and shut down the loop, causing most of the feed solution to be lost. The test was resumed the next morning with fresh feed and without this module. The results of this experiment indicate several notable trends:

1. The membranes formed on the stainless steel tubes were not as stable as those on the ceramic tubes. The initial fluxes and rejections were comparable with those of the ceramics, but shutdowns and contact with the simulated decker filtrate caused marked deterioration. The color and TOC in their permeates were higher than for any of the ceramic tubes, with or without polyacrylate. The rejections obtained with the 0.2 μm tube were considerably higher than those with the 5 μm tube.

2. The tube bundle with only the hydrous Zr(IV) oxide layer gave poorer TOC and color rejections than the other ceramic bundles (before it failed). The membrane exposed briefly to the polyacrylic acid was initially only slightly different from the Zr(IV) – PAA membrane. Its rejections at the end of the run were slightly lower.

3. The fluxes remained favorable at high water recovery, which compares well with the data in Figure 6. However, at a concentrate level of 12% total solids, total sulfur rejection had declined to 69% for the Zr(IV) – PAA membrane, as compared with 85% in Figure 6. The total sulfur rejections shown in Figure 7 under similar conditions are intermediate. The reason for these differences is not clear because rejections at low water recovery levels were comparable.

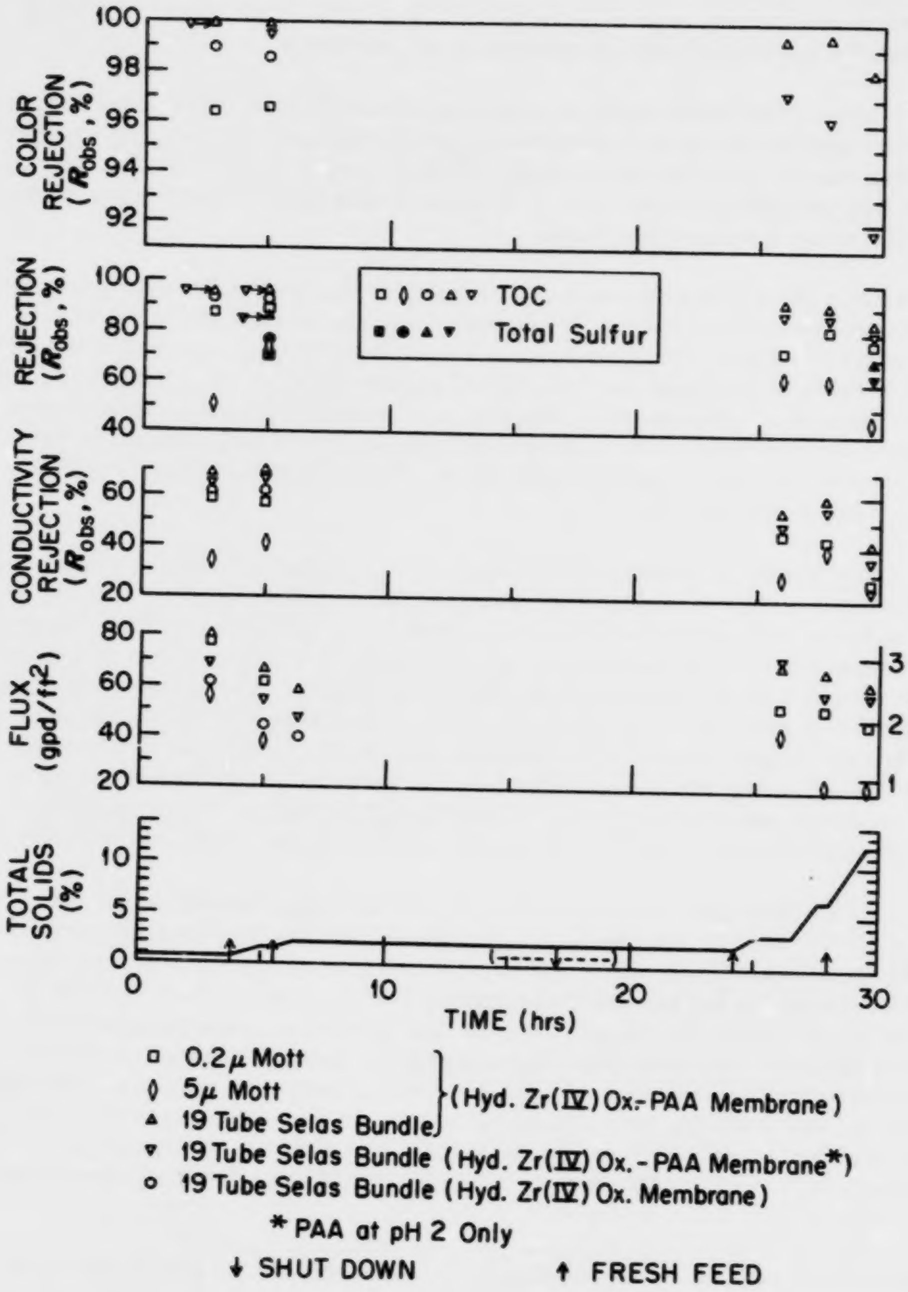


Figure 8. Hyperfiltration of diluted weak black liquor.
(pH 11-12; 15 ft/sec; 950 psi)
(4.6 m/sec; 6.55x10^6 Pa)

It appears that the exposure of the membrane to polyacrylic acid is beneficial. The fluxes of the Zr(IV)—PAA membranes were essentially higher than those of the single layer Zr(IV) oxide membrane. Thus, the use of a polyacrylate overlayer seems worthwhile.

During the course of the overall study, stainless steel tubes with a pore size rating of 0.5 μm were developed by Mott Metallurgical. Test results comparing hydrous Zr(IV) oxide-polyacrylate membranes with a new 0.5 μm Mott tube, a new 0.2 μm Mott tube, an old 0.2 μm Mott tube, and a Selas ceramic tube are summarized in Figure 9. The 0.5 μm tube gave rejections similar to those with the new 0.2 μm but at much higher fluxes.

The variations in performance because of the variations in membrane supports and pH were not the only operating parameters studied. The hydrodynamic environment within the 19-tube module is important in membrane formation because of its effect on concentration polarization and fouling. The flow regime through the Selas module is complicated, and it is difficult to predict the situation for tubes in different positions. However, by comparing rejections and fluxes from individual tubes, it should be possible to detect gross differences. If the concentrated solution velocity over different tubes varies greatly, concentration polarization should result in obvious variations in permeate quality and flux.

In a test with a bundle, originally of 19 tubes but with two broken off, individual tubes were sampled with different overall flow velocities (Figure 10). The membrane condition was monitored over the period of the test by taking composite measurements. As seen in Figure 10, the repeated tests show some membrane deterioration at 4.57 m/s (15 ft/sec), but the concentration polarization effects can still be seen with the lower velocities. The percent rejection is obtained by a comparison of the conductivities of the concentrate and the permeates. The arrows indicate whether the flow entered or exited at the base of the bundle. At the highest velocity of 4.57 m/s (15 ft/sec) the variations do not seem greater than the usual random scatter of data, whereas the variations at 1.22 m/s (4 ft/sec) seem significant. This test indicates that differences in the hydrodynamic environment of individual tubes in the 19-tube bundles are not as great at 4.57 m/s (15 ft/sec).

The design of reverse osmosis systems and the estimates of energy consumption of the processes require information on the dependence of pressure drop through the system components particularly the membrane modules and on circulation velocity. Measurements of pressure drop through a module containing two Selas 19-tube bundles are summarized in Figure 11. Tests at different temperatures showed that the pressure drops were slightly, but probably significantly, lower at high temperatures. The effect of circulation velocity on pressure drop was also noted in previous studies showing that a lower velocity caused a lower pressure drop through a series array of modules. Consequently, the flux from the last few bundles was higher because of the higher applied pressure. However, a balance between lower pressure losses and increased concentration polarization effects must be reached. A circulation velocity of 4.57 m/s (15 ft/sec) seemed to be optimal.

The effect of feed prefiltration was tested using a filter capable of removing particles with diameters as small as 5 μm. Hydrous Zr(IV) oxide-polyacrylate membranes were formed on a Selas ceramic (0.27 μm) tube, and unfiltered and filtered solutions were fed to it. The results, given in Figure 12, indicate that no gains in flux or rejection were obtained with prefiltration. Results with membranes formed on Millipore (0.025 μm pore diameter) and Acropor (0.45 μm pore diameter) film supports are comparable with those obtained on the ceramic tube.

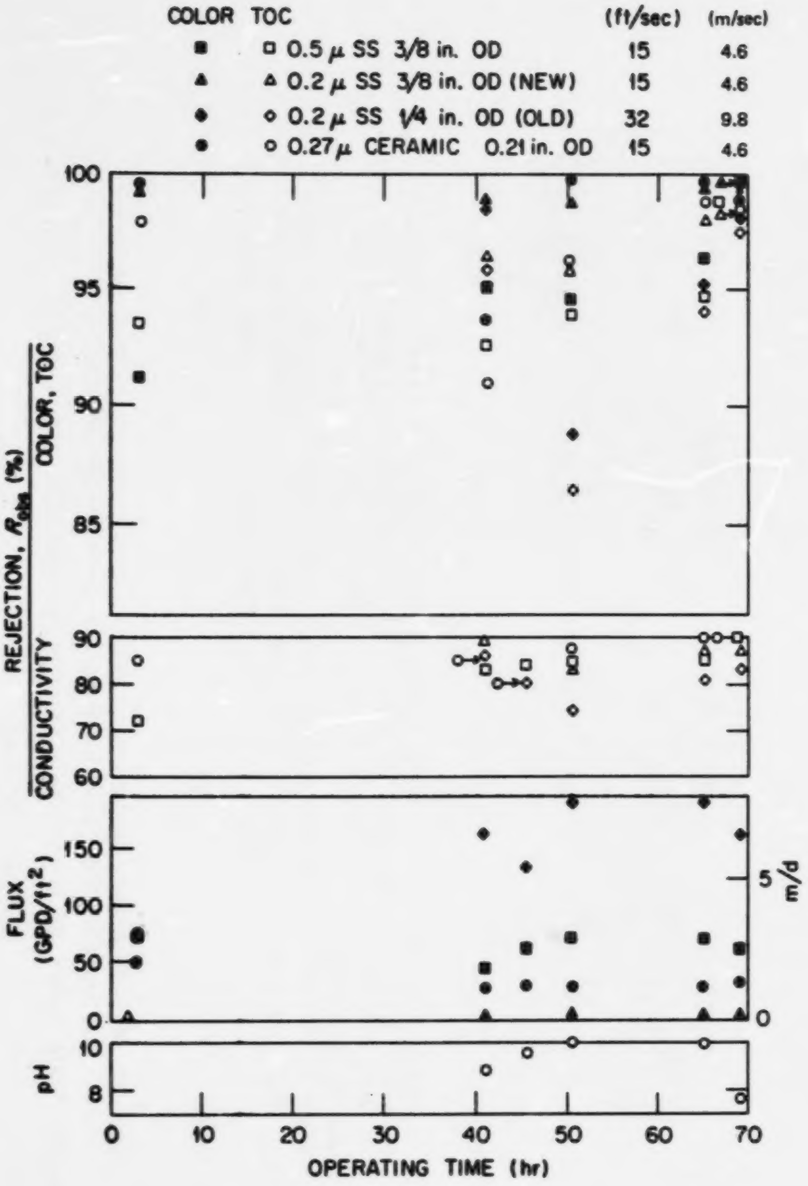


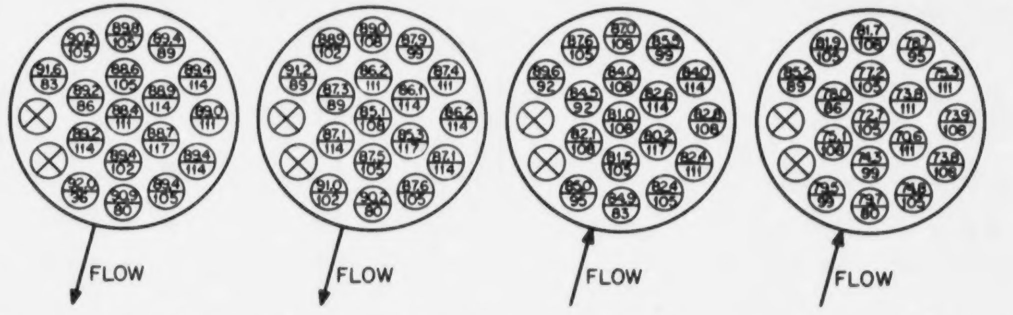
Figure 9. Hyperfiltration of simulated kraft pulp-washing effluent: Mott porous stainless steel tubes and Selas ceramic tube.
[950 psi(6.55×10^6 Pa); 55°C]

15 ft/sec : 98 gpd/ft^2
4.6 m/sec : 4.0 m/d
R_{obs} , 90%

8 ft/sec : 98 gpd/ft^2
2.4 m/sec : 4.0 m/d
R_{obs} , 88 %

8 ft/sec : 98 gpd/ft^2
2.4 m/sec : 4.0 m/d
R_{obs} , 84.5 %

4 ft/sec : 105 gpd/ft^2
1.2 m/sec : 4.3 m/d
R_{obs} , 77 %



15 ft/sec : 101 gpd/ft^2
4.6 m/sec : 4.1 m/d
R_{obs} , 89.5%
Next day, after pH adj.
99 gpd/ft^2 , 4.0 m/d
R_{obs} , 92.5%

8 ft/sec : 98 gpd/ft^2
2.4 m/sec : 4.0 m/d
R_{obs} , 88 %

15 ft/sec : 99 gpd/ft^2
4.6 m/sec : 4.0 m/d
R_{obs} , 91 %

8 ft/sec : 99 gpd/ft^2
2.4 m/sec : 4.0 m/d
R_{obs} , 83.4 %

15 ft/sec : 104 gpd/ft^2
4.6 m/sec : 4.2 m/d
R_{obs} , 86%

4 ft/sec : 105 gpd/ft^2
1.2 m/sec : 4.3 m/d
R_{obs} , 77%

15 ft/sec : 109 gpd/ft^2
4.6 m/sec : 4.4 m/d
R_{obs} , 87%

Order of Tests: (1) (2) (3) (4)

Figure 10. Hyperfiltration of properties of hydrous Zr(IV) oxide-polyacrylate membrane on individual Selas tubes in 19-tube bundle (two tubes broken).

(Composite Tests Before Individual Tube Measurements Given Above, and Just After, Below)

950 psi , 65.5 bar
25° C
pH 7.5 - 8.5
0.05 *M* NaCl

% R_{obs}
gpd/ft^2
⊗ VOID

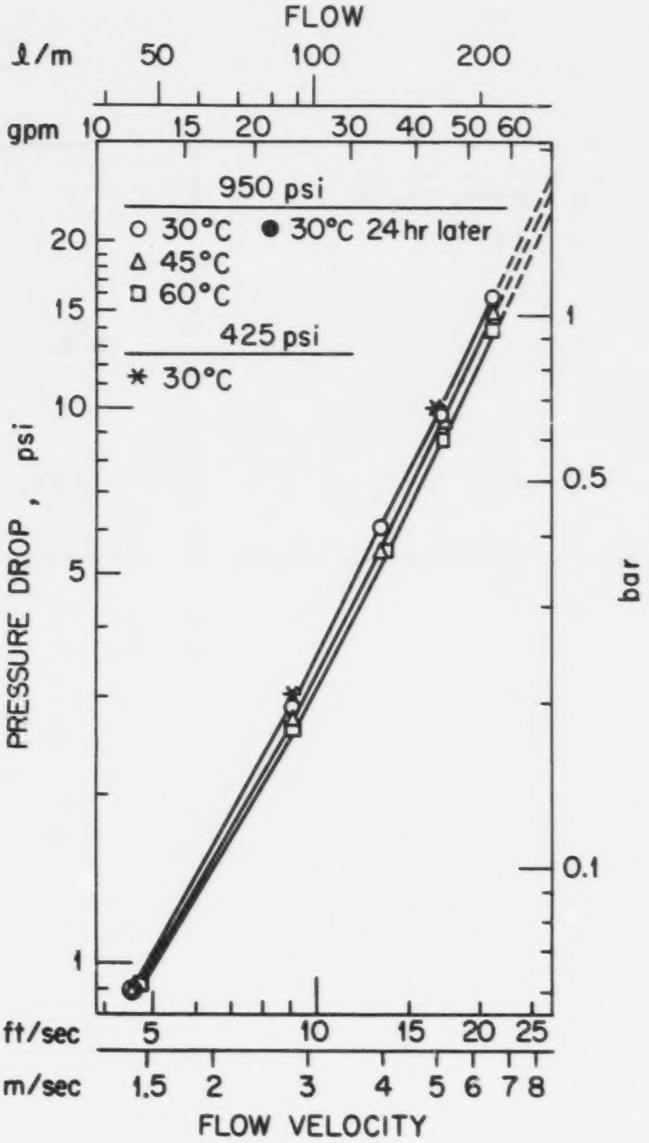


Figure 11. Pressure drop versus flow for Selas module with two 19-tube bundles in place.

(1 gpm ≎ 0.4 ft/sec)
(1 ℓ/m ≎ 0.032 m/sec)

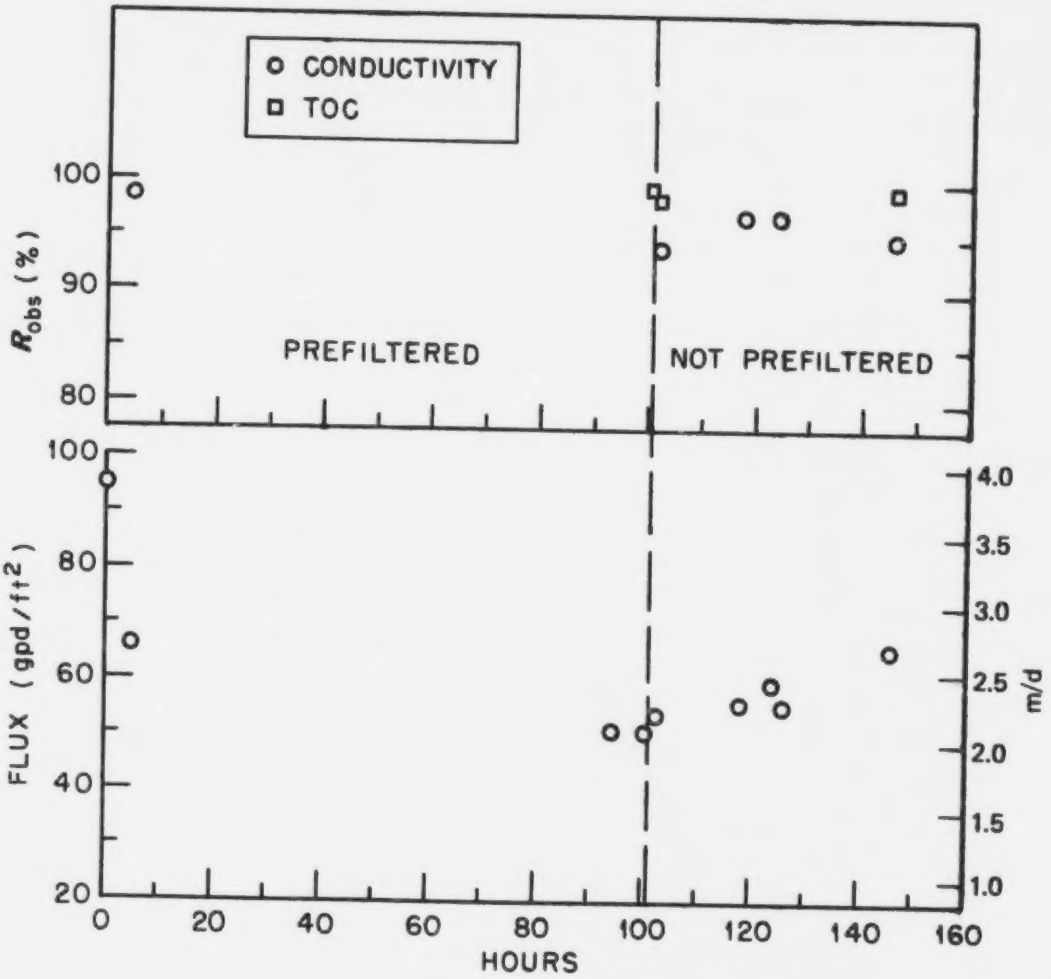


Figure 12. Effect of prefiltration of feed on hyperfiltration of pulp-washing effluent.

(15 ft/sec; 950 psi; 55°C)
(4.6 m/sec; 655×10^6 Pa)

The laboratory tests were made on simulated decker filtrates by diluting shipped-in weak black liquor from a nominal 12 to 15% total solids to about 1% total solids concentration. A possible difference in the laboratory and the actual in-plant feeds is the degree of oxidation of the constituents. An attempt was made to detect such an effect by running a test with the simulated decker filtrate in a two-stage sequence: the first with oxygen bubbled through the feed and the second with no oxygen added. A hydrous Zr(IV) oxide-polyacrylate membrane was formed on a Selas 19-tube bundle, which at the end of formation gave a rejection of 88% at 3.38 $m^3/m^2/d$ (83 gfd) with a 0.05 M NaCl feed. Simulated decker filtrate was introduced to the unit and the permeate was discarded. Fresh feed was added to bring the total solids content to approximately 3% during the first phase. After the oxygen was shut off, the flux and rejection seemed to increase slightly as seen in Figure 13. This increase, however, is masked by the weekend shutdown which occurred at approximately the same time that the oxygen was discontinued.

Other researchers have found enzyme detergents, ethylenediaminetetraacetic acid (EDTA), and trisodium phosphate (TSP) to be useful in cleaning fouling layers from reverse osmosis and ultrafiltration membranes. In tests with naval shipboard laundry wastes, it was observed that the fouling by some feeds could be removed to a large extent by exposure to the synthetic solution approximating the waste. This solution contains Triton X-100, Na_2CO_3, sour, and kaolinite. Its effect on membranes previously exposed to diluted weak black liquor is shown in Figure 14. The washes appeared to be beneficial, but the improvement diminished in successive cycles.

Ultrafiltration

In the flow scheme shown in Figure 15, an extended test of a dual layer hydrous Zr(IV)–Si(IV) oxide membrane was performed using a Selas 19-tube bundle. The results of the test with unneutralized bleach plant caustic extraction effluent (E_1) are shown in Figure 16. Limits on availability precluded the continuous introduction of fresh feed, but at intervals some permeate was discarded and made up with equivalent volumes of fresh feed. Color and TOC removals were good, and chloride was rejected to only a minor degree. This is desirable in this case to prevent recycle and build up of chlorides in the mill chemical recovery system. The flux was still about 1.83 m^3/m 1.83 $m^3/m^2/d$ (45 gfd) after 4 months of operation. A dye-waste study performed during an interruption, reduced the flux, and further exposure to a solution containing silica did not restore it. A wash with a Na_2CO_3 solution brought the flux back up to 1.63 $m^3/m^2/d$ (40 gfd).

Tests were also performed with Mott porous stainless steel tubes using hydrous Zr(IV)–Si(IV) oxide membranes. The Mott tubes were rated as 0.2 and 5 µm and, like the Mott tubes used in the reverse osmosis work, are rated by the particle size filtered rather than the pore diameter. A filter-aid was used with the steel tubes. The rejection of the steel tubes was comparable to that of the ceramic tubes (Figure 17), with the flux from the 0.2 µm tube falling between that of the single ceramic tube and the ceramic bundle. The 5 µm steel tube flux was comparatively low. The comparison between the steel and ceramic tubes is complicated by the different velocities, but the results seem to indicate that a Mott tube of a smaller pore size would be suitable for ultrafiltration of bleach plant effluents.

Newer Mott stainless steel tubes used for reverse osmosis tests were also used for ultrafiltration trials. A hydrous Zr(IV)–Si(IV) oxide layer was formed on the new Mott tubes (0.2 and 0.5 µm), on an old Mott tube (0.2 µm), and on a fresh Selas ceramic tube (0.27 µm) for comparison. The results of the experiments with unneutralized E_1 are shown in Figure 18. Color rejections were

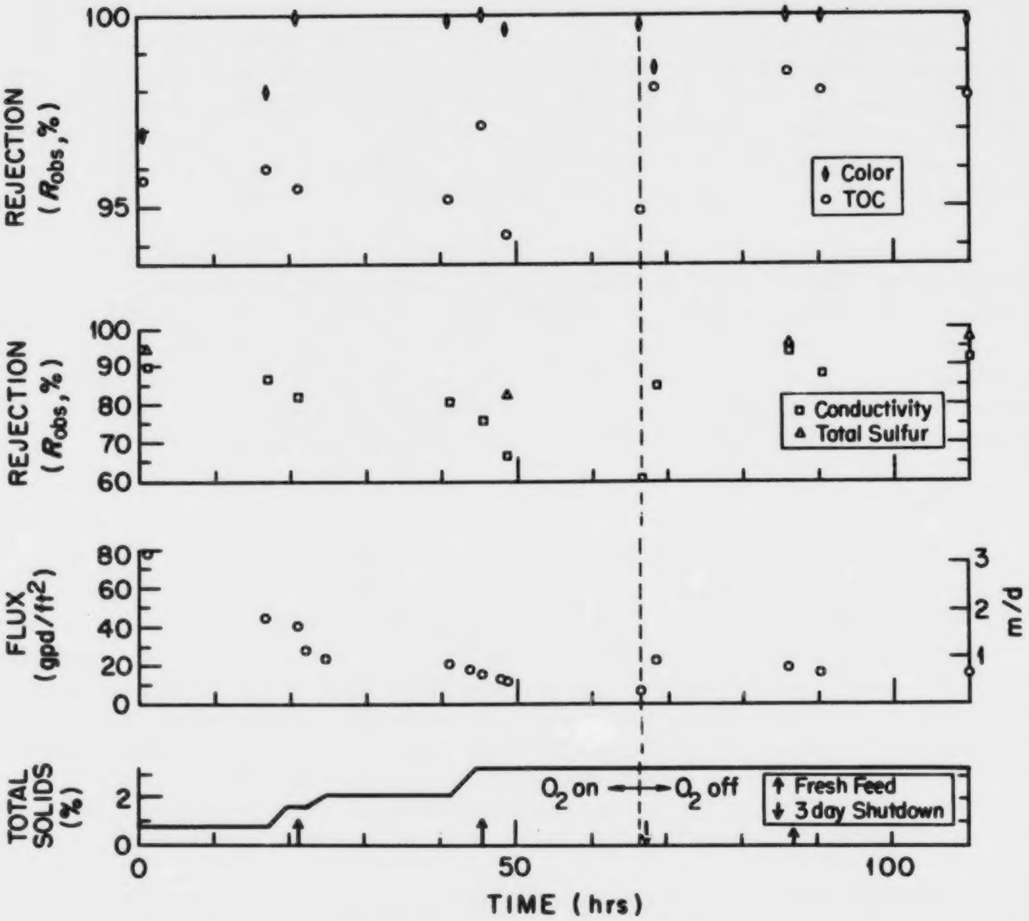


Figure 13. Effect of oxygen on hyperfiltration of simulated pulp-wash liquors.

950 psi 6.55×10^6 Pa	55°C	15 ft/sec 4.6 m/sec	pH 7-8

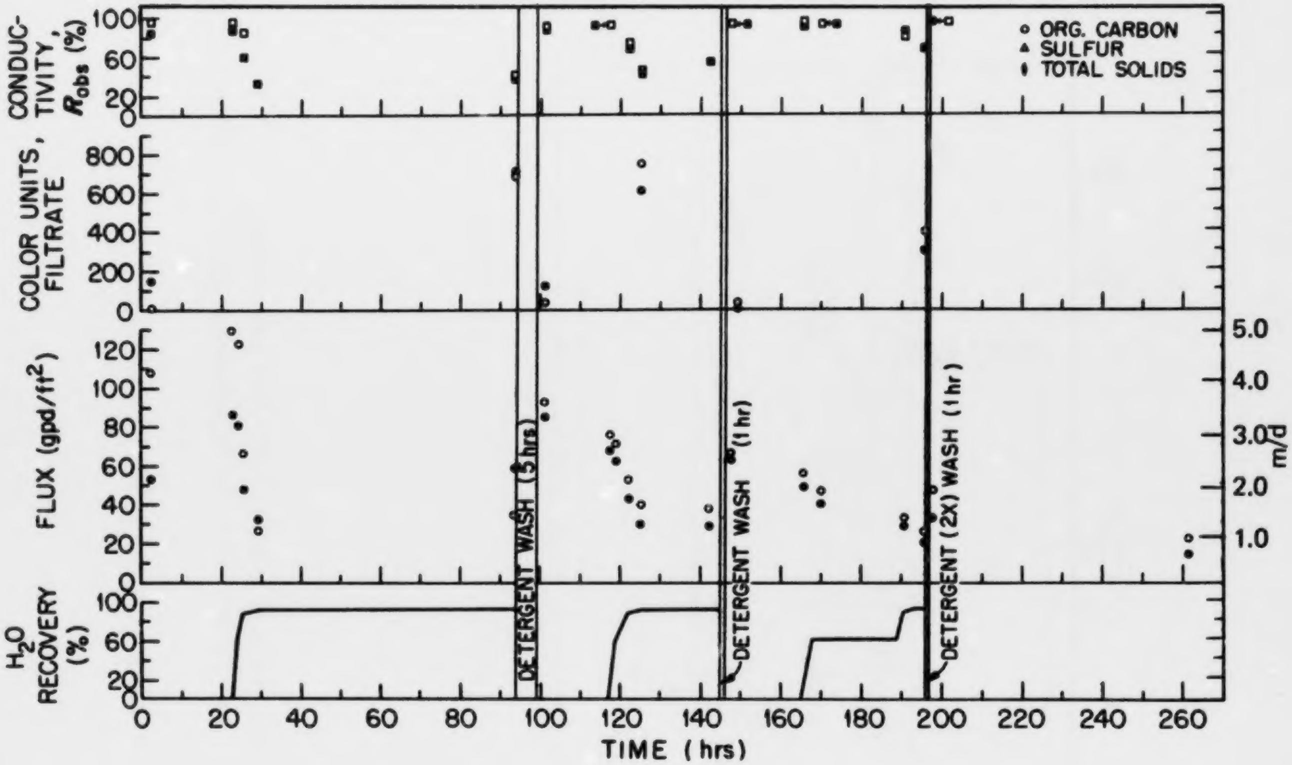
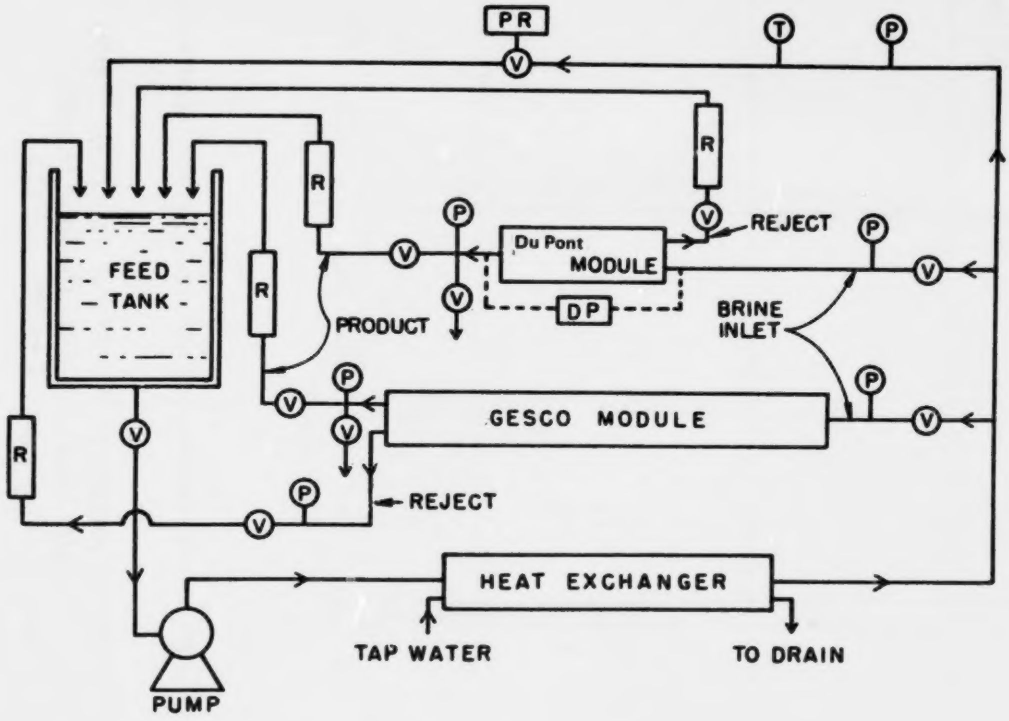


Figure 14. Hyperfiltration of kraft-pulping wash effluents: detergent regeneration.

Hydrous Zr(IV) Oxide-polyacrylate Membrane on 0.27μ Selas Tubes.
Open Points, Single Tube; Solid, 19-Tube Bundle.
(15 ft/sec; 950 psi; pH, 7 to 8.5; 55°C)
(4.6 m/sec; 6.55×10^6 Pa)



DP: Differential Pressure Gauge ; P: Pressure Gauge ;
PR: Pressure Regulator ; R: Rotameter ; T: Temperature Gauge ; V: Valve.

Figure 15. Flow diagram of ultrafiltration loop.

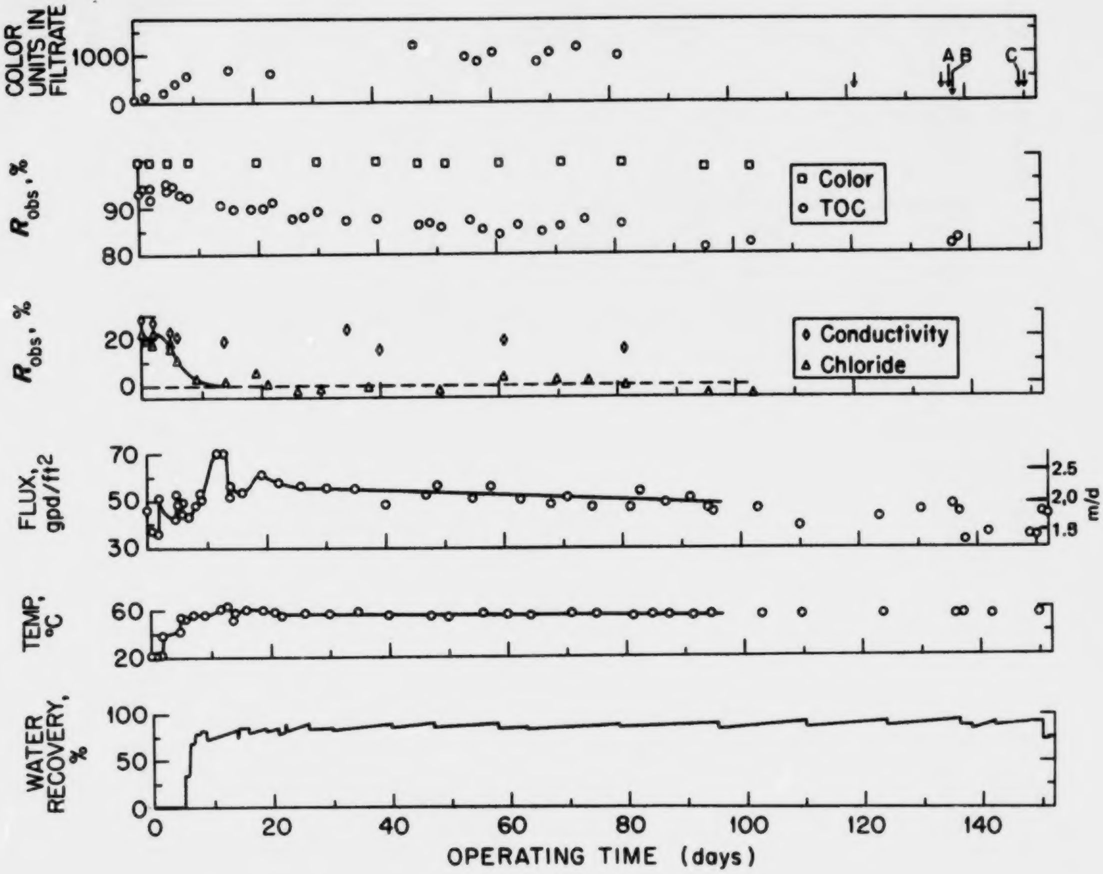
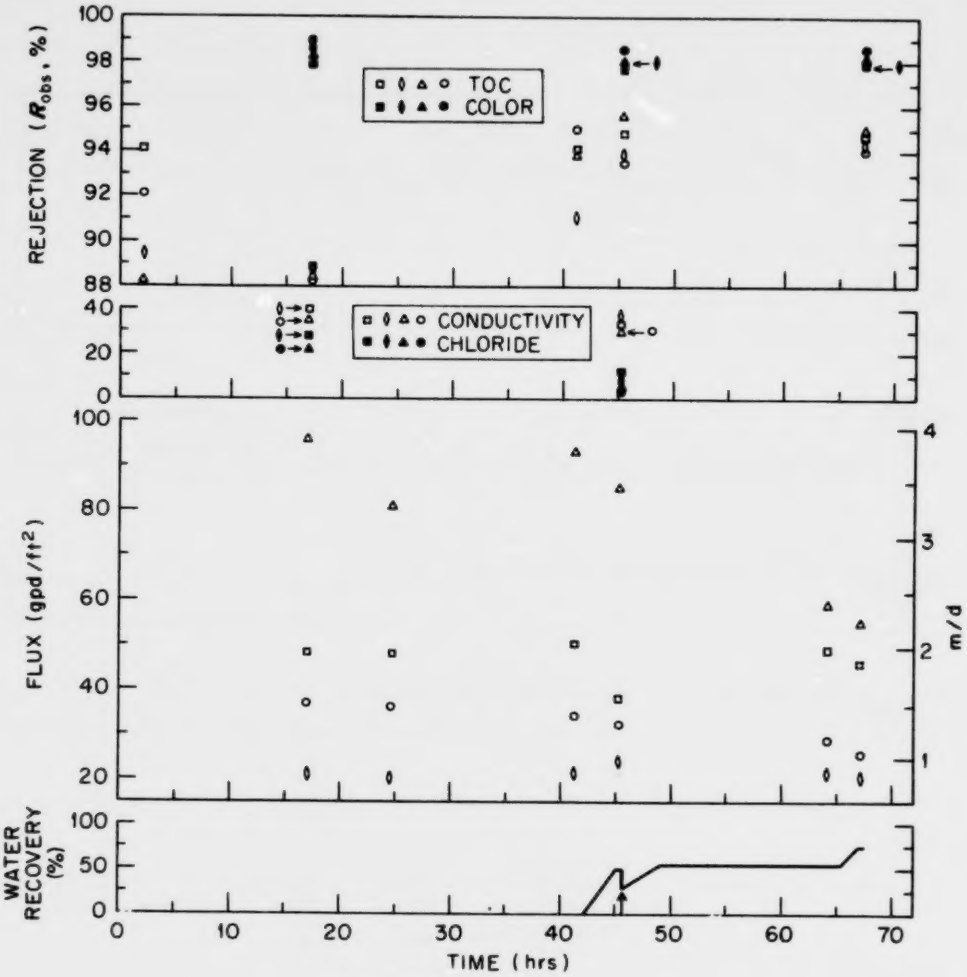


Figure 16. Ultrafiltration of bleach plant effluent by hydrous Zr(IV)-Si(IV) oxide membrane on 19-tube Selas bundle.

(200 psi, 7 ft/sec, pH 8.5 to 9.5)
(1.38×10^6 Pa; 2.1 m/sec)

↓ Shutdowns A. Interruption for Laundry and Dye Waste Tests
B. Silica Coating Renewal
C. Na_2CO_3 Wash



SUPPORT	ft/sec	m/sec
Stainless Steel (Mott)		
□ 0.2μ	11.4	3.5
◊ 5μ	11.4	3.5
0.27μ Ceramic (Selas)		
△ Single Tube	4.7	1.4
○ 19-Tube Bundle	9.8	3.0

↑ FRESH FEED

Figure 17. Ultrafiltration of kraft bleach plant effluents with hydrous Zr(IV)-Si(IV) oxide membranes.

($\frac{200 \text{ psi}}{1.38\times10^6 \text{Pa}}$; 55°C ; pH, 9.8)

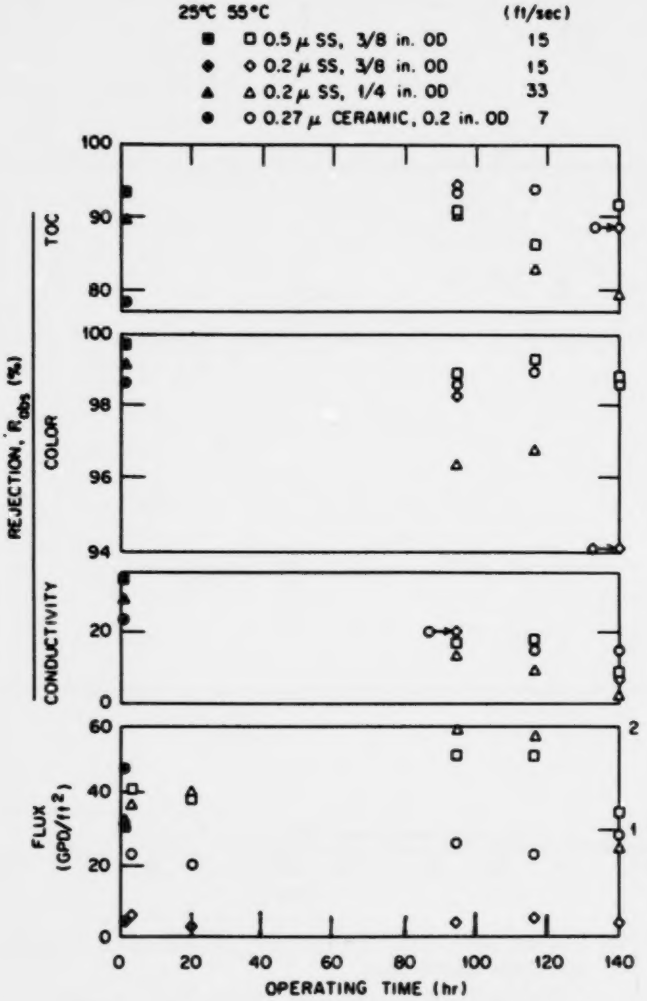


Figure 18. Ultrafiltration of kraft bleach plant effluent by hydrous Zr(IV)-Si(IV) oxide membrane on Mott porous stainless steel tubes and Selas ceramic tube.

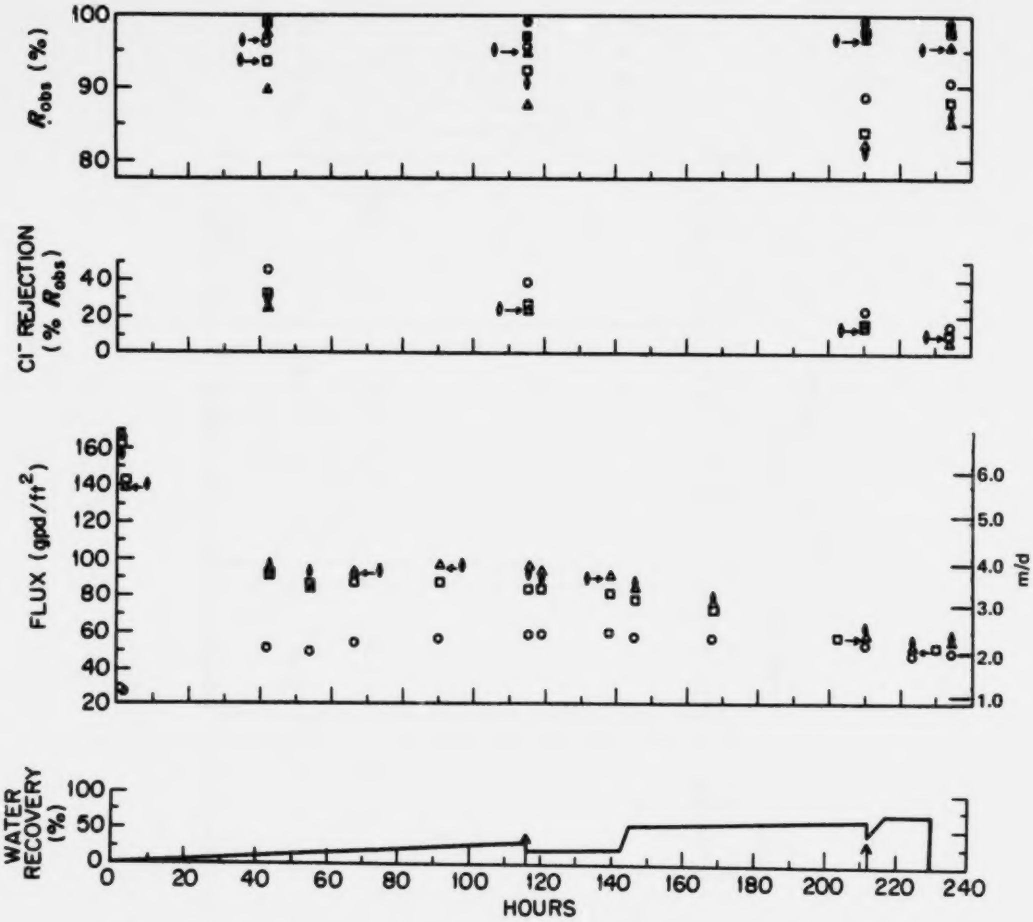


Figure 19. Comparison of ultrafiltration of bleach plant effluent by several dynamic membranes.
(200 psi , 60°C, pH ~9 , 0.27μ Selas Ceramic)
(1.38x10⁶ Pa)

Support	Membrane	ft/sec	m/sec	Rej.	
				TOC	Color
19-Tube Bundle	Hydrous Zr(IV)-Si(IV)Oxide	5.7	1.7	○	●
Single Tube	Pluronic 25R2	6.6	2.0	△	▲
Single Tube	Pluronic 25R5	6.6	2.0	□	■
Single Tube	Pluronic 25R8	6.6	2.0	♦	♦

greater than 98%, except for the old 0.2 μm Mott tube, and the flux rate for the Mott 0.5 μm tube was greater than for the new Mott 0.2 μm tube. Unfortunately, the time limit prevented incorporation of any new Mott tubes into the pilot plant operation.

In an earlier section, this report states that a dynamically formed membrane of block copolymers of polyethylene oxide-polypropylene oxide appeared promising for the ultrafiltration of bleach plant effluents. The polymer tested earlier was part of a class marketed as Pluronics by the Wyandotte Corporation. Later trials with other members of this group were undertaken using Selas ceramic tubes, and the results are shown in Figure 19. The designations in the key of Figure 19 are from the manufacturer's literature. They refer to the molecular weight of the propylene oxide portion of the molecule (25 is equal to molecular weight 2500), the position of the polypropylene oxide structures on the molecule chains (R), and the approximate weight percentage of the polyethylene (5, for example, stands for 50%). The code seems to include considerable approximation, but the membranes listed in Figure 18 show a range of hyrophilic properties.

The Selas 19-tube bundle (with a hydrous Zr(IV)–Si(IV) oxide membrane) was the same one used for previous ultrafiltration tests. The inorganic membrane generally gave higher rejections than the Pluronics. The fluxes from the organic membranes were higher initially, but tended toward the same values as the inorganic membrane obtained at the end of the run. There was no clear trend of flux or rejection variations when polyethylene oxide content was increased. The increase in flux through the hydrous Zr(IV)–Si(IV) oxide membrane was probably caused by a recovery from exposure to highly fouling tannery wastes used in previous tests.

In addition to the Pluronics polymeric membranes, samples of biopolymers marketed by the Kelco Corporation were tested. They have properties somewhat different from the other additives, as the Kelgins are alginic acids. One Kelco biopolymer designated MV is of intermediate molecular weight as indicated by viscosity, and another designated XL is of low molecular weight. Kelzan is a xanthan gum with a molecular weight of about 2 million. The material used was more highly refined than the grade used to enhance oil recovery. Kelzan is interesting because its chains are said to possess unusual stiffness, and little change in the viscosity of its solutions because of salt concentration or temperature can occur. The results of the ultrafiltration tests with these additives are summarized in Table 3. The organic polymers had been originally formed on single Selas ceramic tubes for reverse osmosis tests from a 0.05 $\underline{M}$ NaCl solution. The hydrous Zr(IV) – Si(IV) oxide membrane was on a Selas 19-tube ceramic bundle used in previous ultrafiltration tests. The data in Table 3 were taken after only 3 hours of operation but are similar to those obtained after overnight operation. The properties of the organic membranes were not significantly different from those of the inorganic, except that the inorganic had higher fluxes and rejections of color and TOC. These results did not indicate any obvious advantage of the Kelco or the Pluronic polymers over the hydrous oxides.

In comparing reverse osmosis treatment of simulated decker filtrate with ultrafiltration of bleach plant effluent (E_1) using hydrous Zr(IV) – Si(IV) oxides, it was observed that fouling seemed to be less of a problem in the ultrafiltration trials. The simulated decker filtrate usually contained three to ten times as much of the potentially fouling constituents as the E_1, if TOC and total solids are any indication. Thus, it is possible that the difference in fouling was caused by the differences in feeds, rather than membrane properties. An indication that this is at least partly the cause is seen in Figure 20, in which an ultrafiltration trial with both feeds is summarized. The flux recovered when the feed was changed from simulated decker filtrate to bleach plant effluent. This comparison was partially biased because the simulated decker filtrate had been neutralized prior to the test, and it was noted in later work that reactions of the feed constituents with the sulfuric acid used for pH adjustment can produce species which adversely affect membrane performance.

TABLE 3. ULTRAFILTRATION OF BLEACH-PLANT EFFLUENTS BY MEMBRANES, DYNAMICALLY FORMED OF KELCO BIOPOLYMERS
(0.27 μ Selas ceramic tubes)

	Kelgin MV	Kelgin XL	Kelzan	Hydrous* Zr(IV)-Si(IV) Oxide
Hyperfiltration properties (0.05 M NaCl, 950 psi, 15 ft/sec, 25°C, pH ~7)				
Flux, gpd/ft^2	200	100	45	
$\underset{\sim}{R}_{\text{obs}}$, %, conductivity	47	67	75	
Ultrafiltration of bleach-plant effluent (200 psi, ~6 ft/sec, 55°C, pH ~9)				
Flux, gpd/ft^2	84	86	52	80
Filtrate Analysis				
TOC, ppm	48	46	41	28
$\underset{\sim}{R}_{\text{obs}}$, %	92	92	92	95
Color units	100	125	110	8
$\underset{\sim}{R}_{\text{obs}}$, %	98	97.5	98	99.8
Chloride, molarity	0.012	0.0093	0.0088	0.012
$\underset{\sim}{R}_{\text{obs}}$, %	22	39	43	20

*19-tube bundle. Other test sections single tubes.

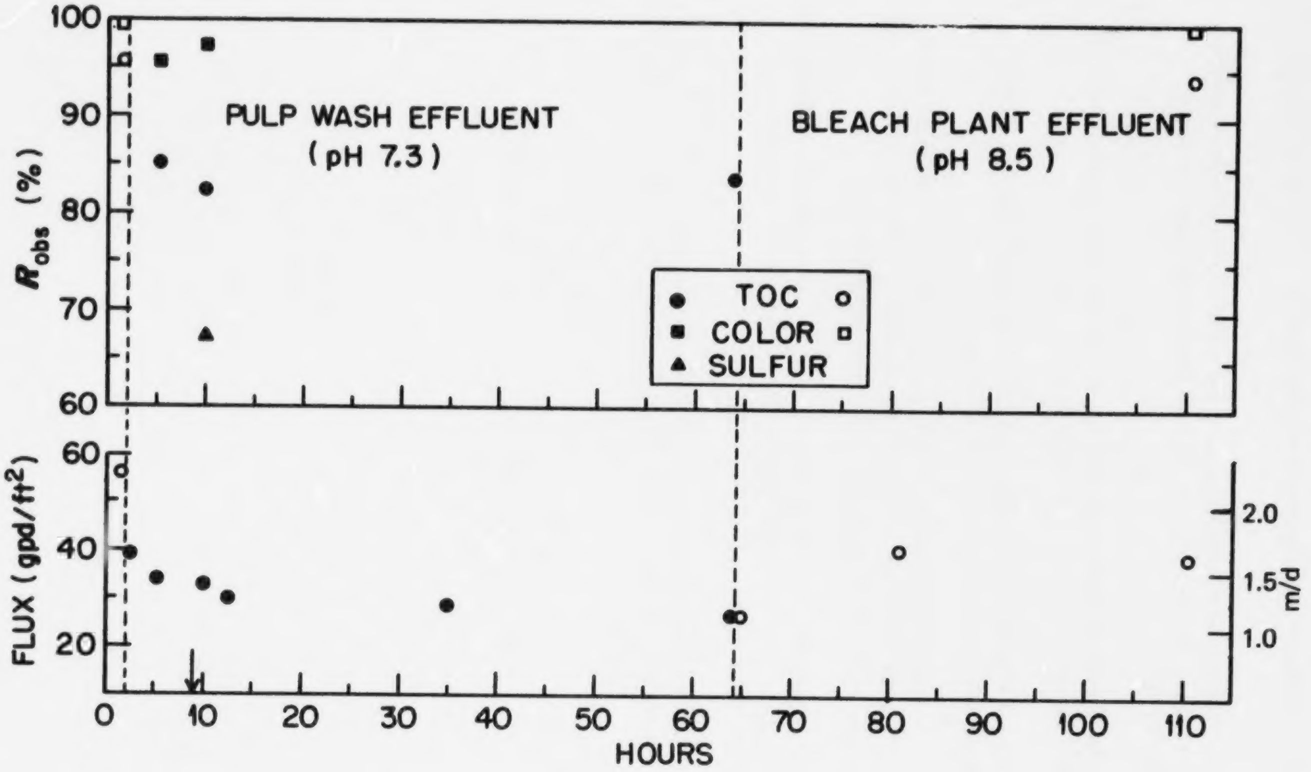


Figure 20. Comparison of ultrafiltration and kraft pulping of effluents.
Hydrous Zr(IV) oxide membrane on 19-tube Selas ceramic bundle.

(5.6 ft/sec ; 200 psi ; 60°C ; ¦ Water Rinse)
(1.7 m/sec; 1.38x10^6 Pa)

Summary

The laboratory tests resulted in several conclusions that were applied to the design of the pilot plants.

1. The most desirable combination of processes and waste waters to be treated is reverse osmosis treatment of decker filtrates and ultrafiltration of bleach plant caustic extraction stage effluent (E_1).
2. The best dynamic membrane for reverse osmosis known at this time is a dual layer of hydrous zirconium(IV) oxide and polyacrylic acid (Zr[IV] – PAA).
3. The best dynamic membrane for ultrafiltration appears to be a dual layer of hydrous zirconium (IV) and silicon (IV) oxides (Zr[IV] – Si[IV]).
4. The most favorable membrane support at the time the pilot plant was designed was the Selas ceramic tube. The Mott stainless steel tubes then available were too unstable and required filteraids. Steel tubes developed later had better characteristics.
5. In extensive tests using various circulation velocities and comparing the resulting fouling, concentration polarization, pressure drops, and fluxes, a velocity of 4.57 m/s (15 ft/sec) was a good compromise.
6. No adjustment of pH is necessary as long as the pH does not stay above 10 while using the Zr(IV) – PAA membrane. High pH is less critical to the Zr(IV) – Si(IV) membrane.

PILOT PLANT STUDIES

The reverse osmosis and ultrafiltration pilot units were constructed at Oak Ridge National Laboratory and shipped to International Paper Company's Mobile, Alabama mill. The units were subsequently moved to the Company's Moss Point, Mississippi mill, which produces a variety of bleached hardwood and softwood products. The units were located inside the pulp mill screen room, with all power, instrument air, fresh and waste water feeds supplied to this location. The reverse osmosis unit was installed to treat combined excess filtrate from the softwood and hardwood decker units, which are the last pulp washing and thickening units before the pulp is transported to the bleaching sequence. The ultrafiltration unit was installed to treat the excess wash water from the caustic extraction stage in the bleach plant sequence and was piped to receive flow from both the hardwood and softwood lines to ensure flow if one bleach line was not operating.

Equipment Descriptions

Reverse Osmosis Unit — —

The reverse osmosis unit is a modified version of a desalination pilot plant used by Oak Ridge National Laboratory for tests performed for the Office of Saline Water at the brackish water facility in Roswell, New Mexico (see Figures 21 and 22). The system consists of a 1.14 m^3 (300 gallon) stainless steel storage tank, a Gaso positive displacement pump (model 3466), and a stainless steel piping loop arranged to hold 32 Selas 19-tube and 12 Selas 61-tube bundles (only the former were used). The storage tank is equipped with drains, an overflow outlet, recycle lines for both concentrate and permeate, and water level controls to turn off the pump at excessively low levels. The operating level is maintained by controlling raw waste water (decker filtrate) feed to the tank. The pump is capable of about 7.89×10^{-3} m^3/s (125 gpm) at 2.07×10^7 Pa (3000 psig) using a 5.6×10^4 watt (75 hp) motor, although the actual operating pressure was limited to 6.894×10^6 Pa (1000 psig). The pump was equipped with a Greer Pulse-Tone™ surge dampener to smooth out pumping pulsations. The piping is arranged in a continuous loop, with the valving configuration designed to arrange the tube bundles into groups of eight. Each group is comprised of two parallel series of four bundles (see Figures 23 and 24). When fully loaded with 32 bundles, the surface area available for membrane formation is about 3.72 m^2 (40 sq ft). A single pass heat exchanger was used to hold the temperature constant. Also, low tank level, high temperature, high and low pressure, and safety pump cutoffs were installed to protect the pump and other system components. The concentrate flow from the pump can be controlled to produce the desired flow velocity (4.57 m/s [15 ft/m]) across the tubes, and may be either discarded or recycled to the storage tank. The permeate could be individually or collectively recycled or discarded, or any individual bundle could be isolated. The mode of operation used here was to recycle the concentrate and discard the filtrate.

Ultrafiltration Unit — —

The ultrafiltration unit (Figure 25) consists of three sections: a 0.76 m^3 (200 gallon) Nalgene storage tank, the pump, and the piping which held the tube bundles. The storage tank is equipped with drains, low and operating level controls, overflow line, and feed and recirculation lines. The feed line supplies fresh caustic extraction stage (E_1) waste water from the bleach plant, and the recirculation lines allow recycle of either/or both permeate and concentrate to the tank. The operational method was to recirculate the concentrate and discard the permeate. The pump was a 2.238×10^4 watt (30 hp) Goulds model 3933 multistage centrifugal pump, equipped with Noryl 2 (fiberglass reinforced plastic) impellers, and capable of flows of up to 0.19 m^3/min (50 gpm) at

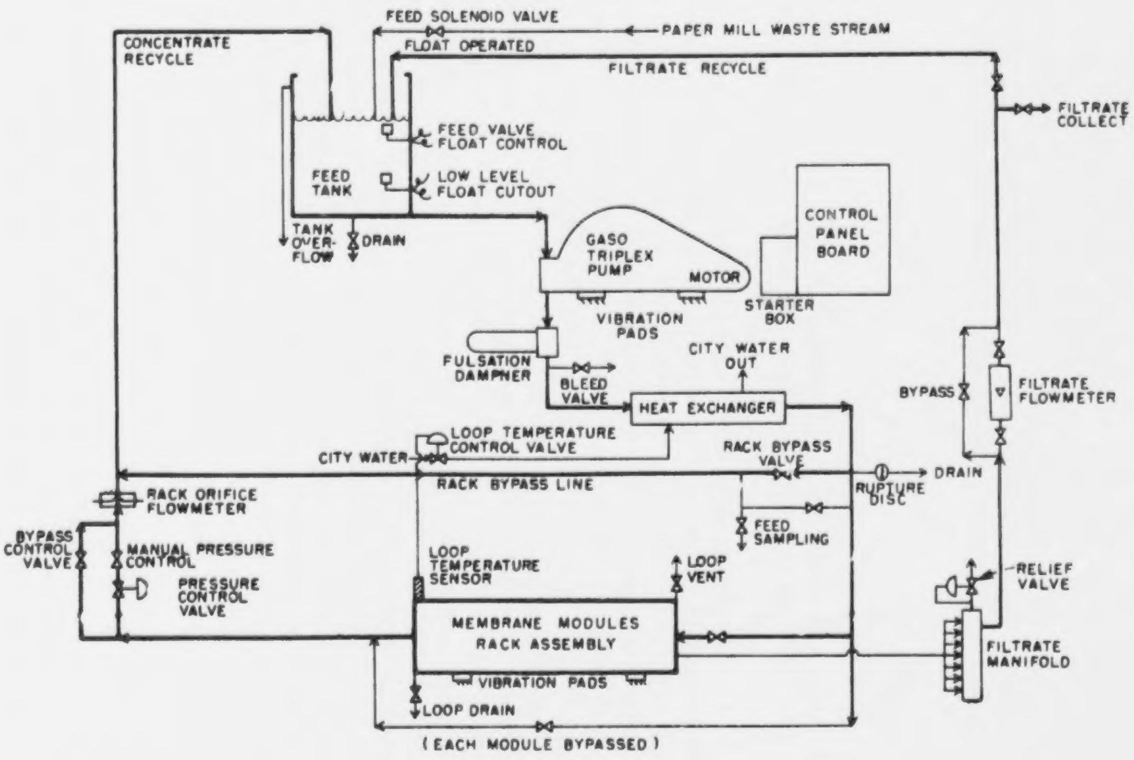


Figure 21. ORNL-IP Co. hyperfiltration loop schematic.

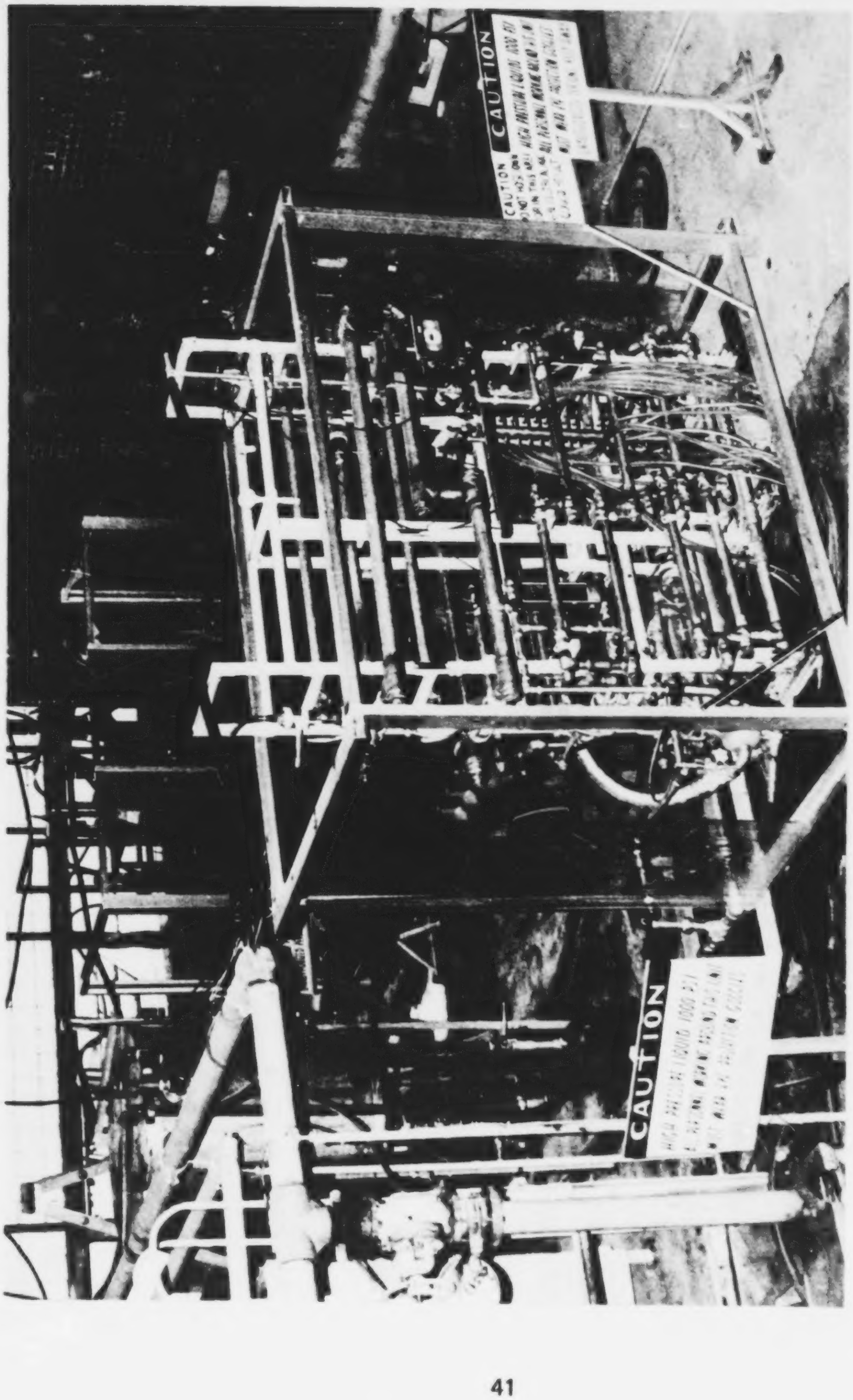


Figure 22. Pilot plant installation. Foreground—reverse osmosis (hyperfiltration) unit; background—ultrafiltration unit.

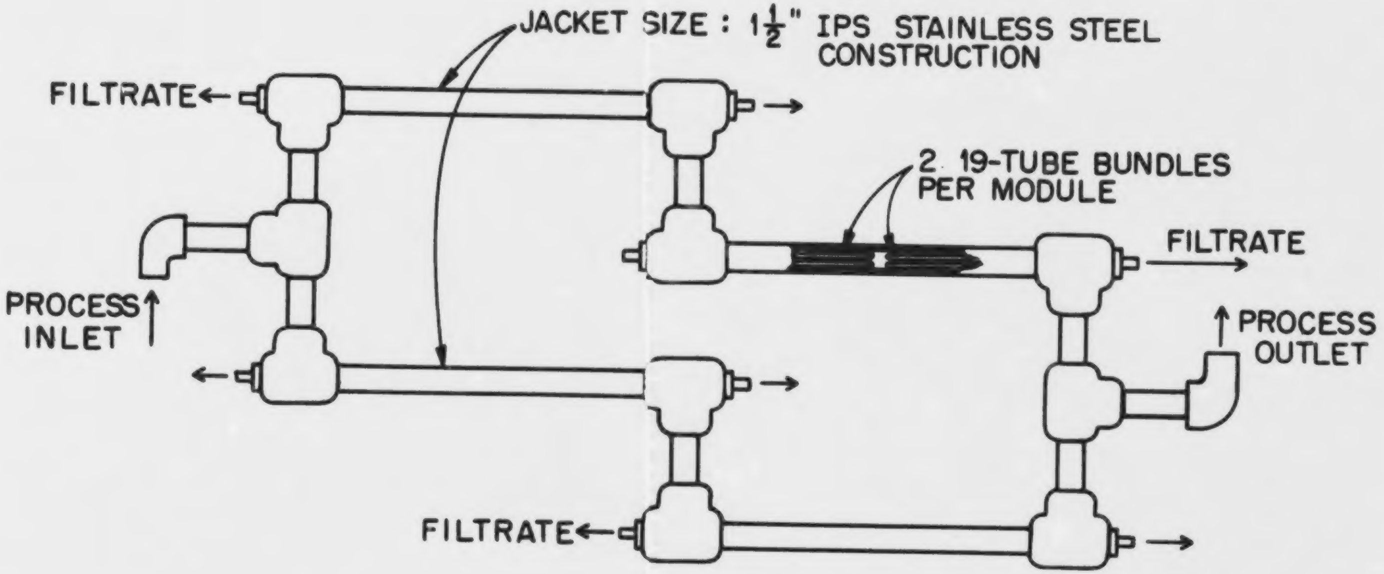

JACKET SIZE : 1½" IPS STAINLESS STEEL CONSTRUCTION
FILTRATE
2 19-TUBE BUNDLES PER MODULE
FILTRATE
PROCESS INLET
PROCESS OUTLET
FILTRATE

Figure 23. Hyperfiltration module assembly containing eight 19-tube bundles: four assemblies in rack.

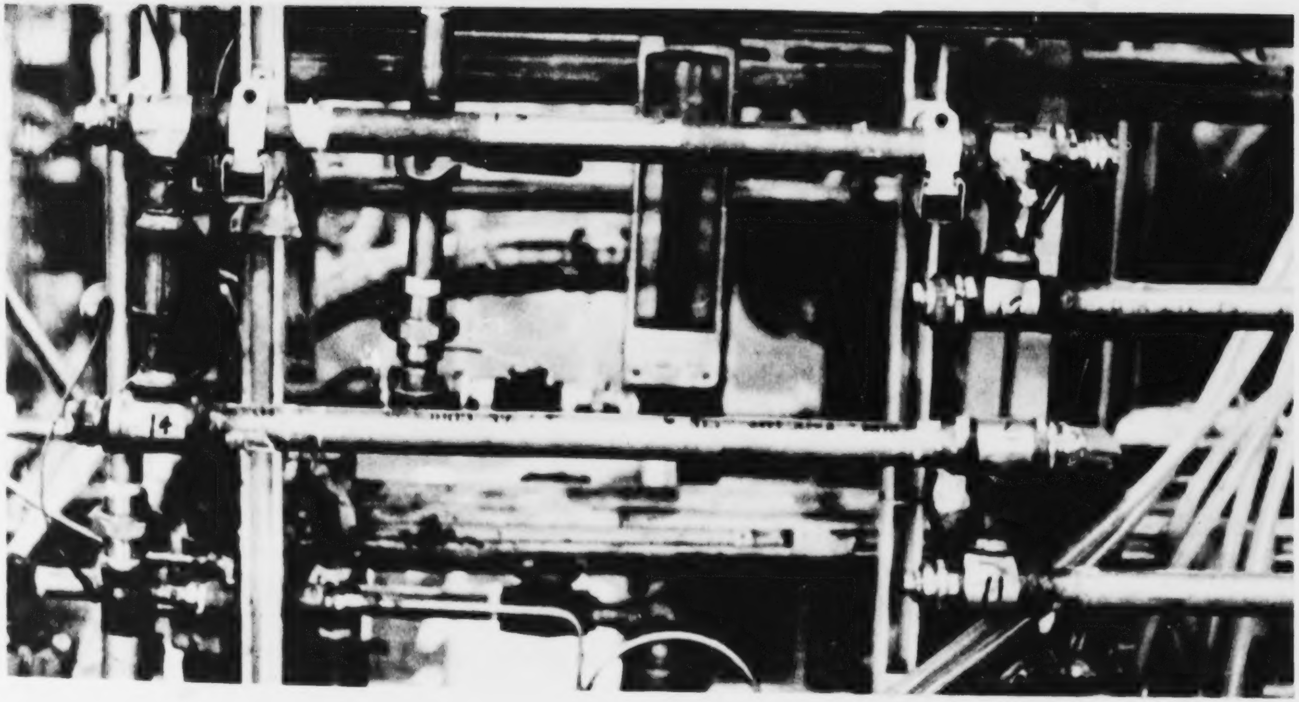


Figure 24. Close-up of reverse osmosis unit.

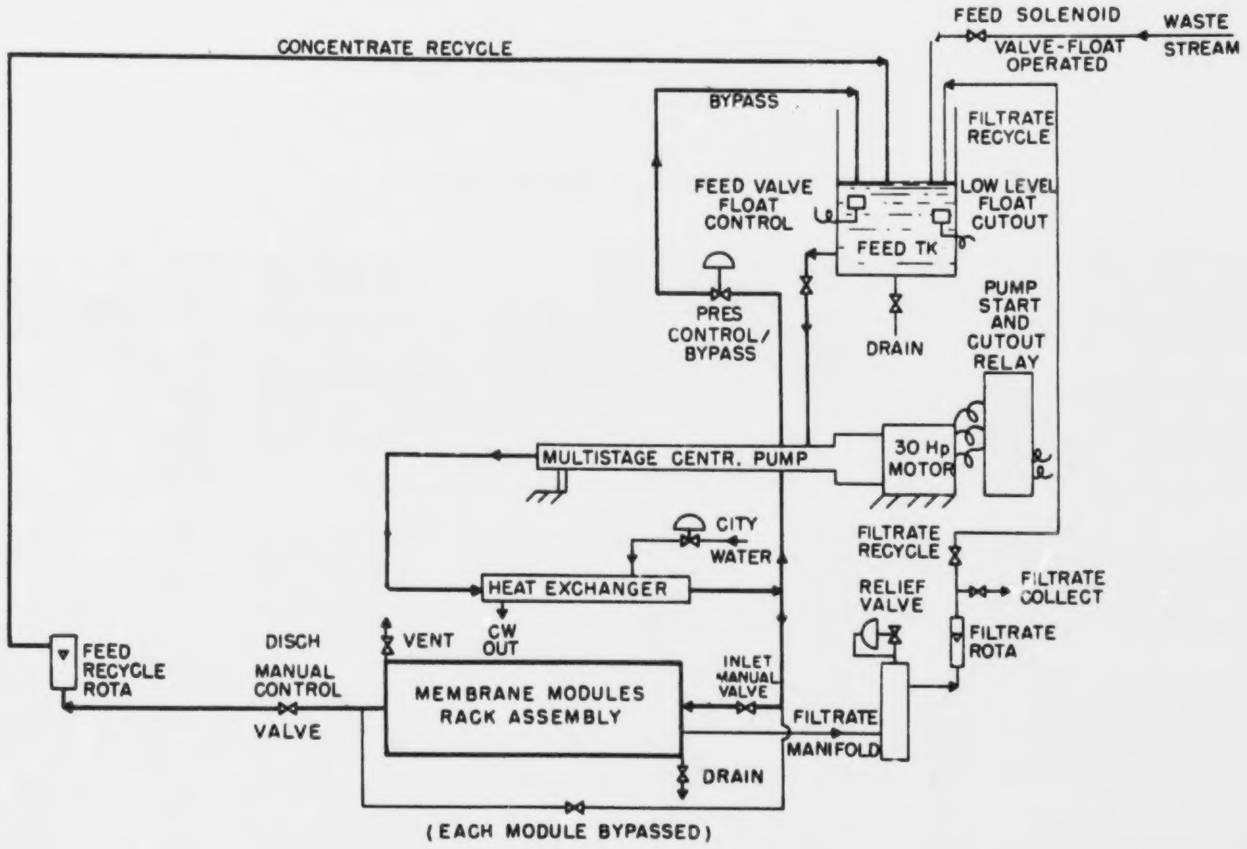


Figure 25. IP ultrafiltration loop schematic.

pressures up to 5.52×10^6 Pa (800 psig). The pump was protected by cutoff controls for high and low operating pressure, high temperature, high and low flow, and low tank level. The waste water was pumped through a single pass heat exchanger for temperature control and into the piping array. The piping was designed to hold sixteen 19-tube bundles in series in groups of four, in a configuration similar to that used in the reverse osmosis unit. The valving allows bypass of any group of four bundles. In addition to the Selas tube bundles, provision was made to accommodate a Union Carbide UCARSEP™ module and an experimental module using Union Carbide carbon tubes.

Operating Experiences

The two units were completely separate but had several common operational characteristics. The two pilot units employed tube bundles for membrane supports comprised of 19 Selas ceramic (0.27 μm) tubes. The tubes were 0.53 cm (0.21 in) O.D. and 33 to 38 cm (13 to 15 in) long, with one end open and embedded in epoxy and the other plugged with polypropylene plugs and fastened into a spacing web to keep tube surfaces separated (see Figure 26). The membrane was formed on the outside, and the permeate passed through the tubes into the fitting in which the bundle was embedded. The total surface area for a complete bundle was 0.11 to 0.13 m² (1.2 to 1.38 sq ft), respective to the varying tube length.

The units were connected to a common power source in the pulp mill, and the frequent power outages that occurred shut down both units. The pilot plants did not have provisions for automatically restarting, so they would remain idle until someone arrived to restart them. Thus, an intermittent power stoppage could shut down both pilot plants for a period of a day or a weekend.

The pilot units were provided with systems to control pH, using sulfuric acid for the reverse osmosis unit and acidic chlorination stage bleach plant effluent for the ultrafiltration unit. These were provided to protect the stability of the membranes, especially the hydrous Zr(IV) oxide-polyacrylate, and to minimize deterioration of the ceramic tubes. However, neither system was used because the pH of both waste waters tended to stay below 10, except for brief increases to approximately 11 with the bleach plant effluent. The tube formulation was adjusted by Selas to make the ceramic tubes compatible with the hot alkaline solutions.

The waste waters fed to both units contained much higher concentrations of pulp fibers than anticipated, compared with the laboratory simulated waste waters. The Oak Ridge National Laboratory personnel concluded that no prefiltration was necessary, based on their experience with the laboratory tests. The waste water used for most of the laboratory studies was diluted weak black liquor which had been shipped by truck in a 55-gallon drum. The actual fiber load in the process waste water was never seen, as the solids had settled in transit. The decker filtrate would tend to have more fibers in it because the washing process involves vacuum dewatering on a rotating screen and because pulp spills in the screen room are washed into the decker filtrate sumps during cleanup. These fibers tended to collect on the spacing web at the end of the bundle, blocking off the openings. The flow path was then progressively altered as fibers accumulated within the interstitial spaces inside the bundle, filling the spaces and covering part of the membrane surface (see Figure 27). In addition, the trapped fibers and reduced flows within the bundles were conducive to biological growth, especially during periods when the unit was shut down. Microscopic examination of the slime found in a tube bundle showed evidence of bacterial and flagellated

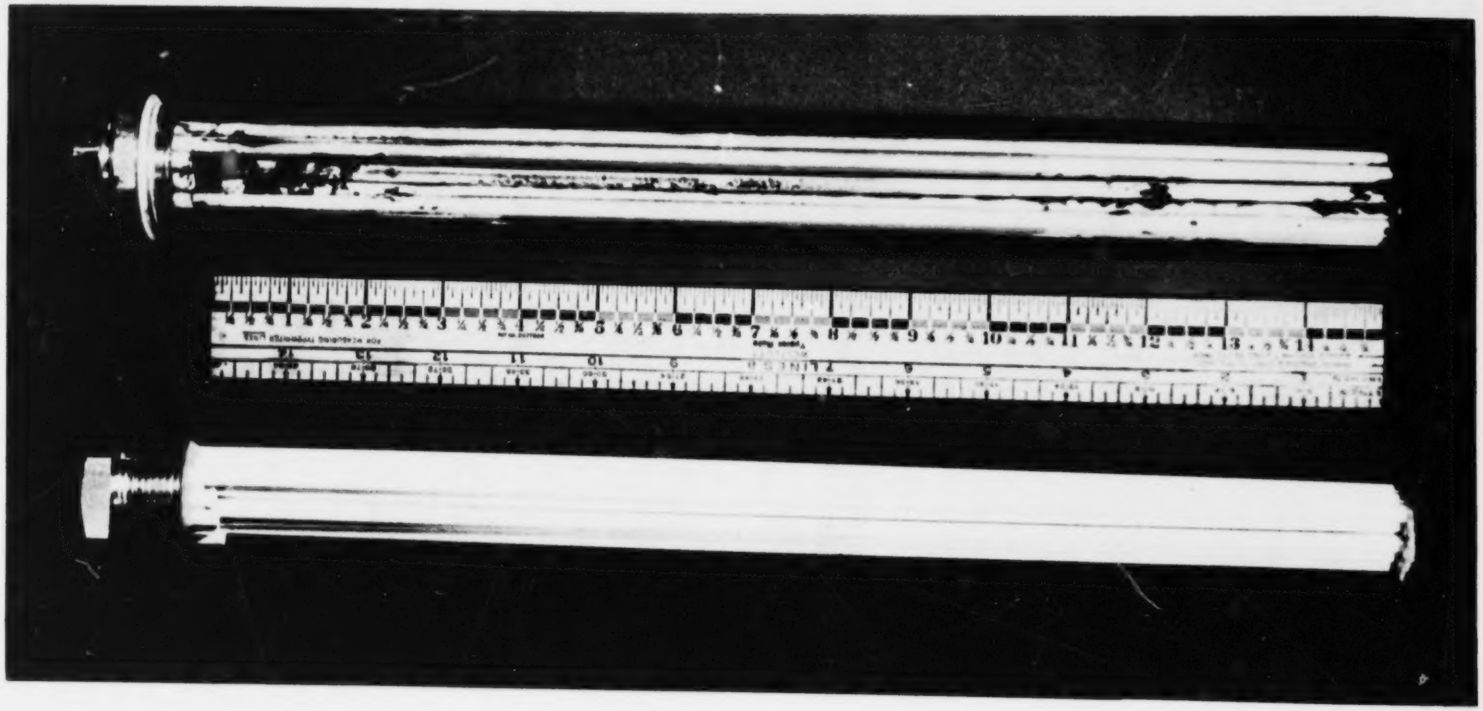


Figure 26. Selas ceramic tube bundles.
Top—used bundle with fiber accumulation; bottom—new bundle with several tubes broken off.

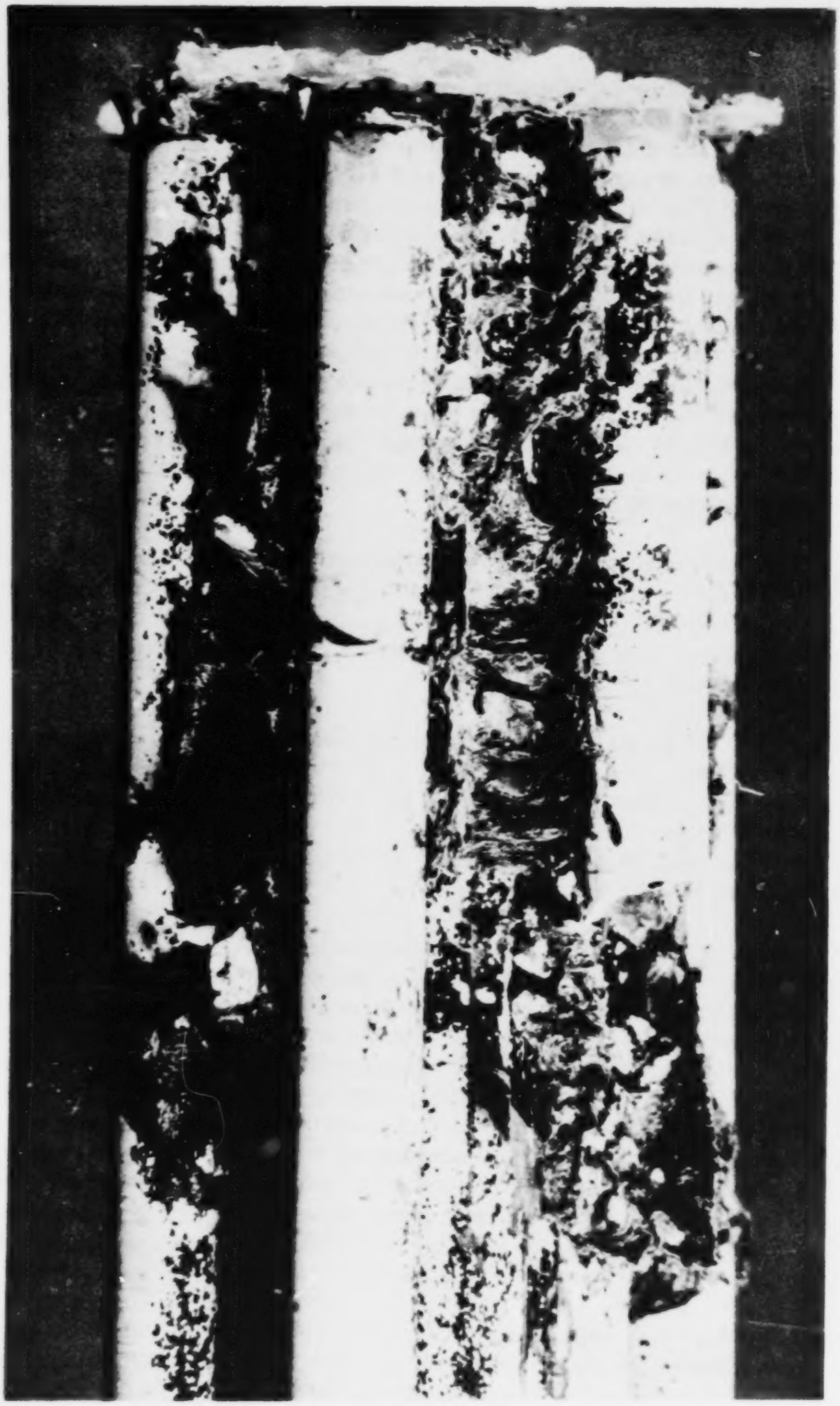


Figure 27. Broken tube bundle with moderate fiber accumulation.

protozoan populations. These microorganisms have apparently adapted to conditions within the pulp mill and were able to survive the high temperature, pressure, velocities, and pH conditions encountered in the tube bundles, once the fiber build up provided them with a substrate.

A critical operational problem of both units was the tube breakage encountered when loading and operating. The tube size, arrangement in the bundle, and the piping size (into which the bundles were loaded) were coordinated to provide as even a flow throughout the bundle as possible. The outer ring of tubes were very close to the inside of the piping in order to force the flow into the interior of the bundle. The bundles were cemented into machined-out threaded reducing plugs and screwed into tees on the ends of the module piping (see Figures 26 and 28). Many bundles were broken and had to be patched or replaced because of outer ring tube breakage during the screwing of these plugs into the tees. Often, bundles were broken during membrane formation and operation and had to be removed or simply isolated. A broken bundle can be critical during membrane formation because the flow of clear concentrate through a broken tube into the common filtrate manifold will falsely indicate a high flux rate and cause the operator to allow a thicker than desired membrane to form. This is important because the overall flux rate is a parameter in judging when the hydrous Zr(IV) oxide layer formation is complete. A broken bundle during actual operation is more easily detected because the permeate flow will increase and the dark concentrate will color the clear permeate.

Unfortunately, a broken bundle cannot simply be isolated and forgotten, especially with the high pressure reverse osmosis unit, because broken tubes tend to break away from their bundles. They are then forced through the piping from bundle-to-bundle breaking more tubes until all the bundles are broken, or bits of tubes are trapped in the piping, completely blocking the flow and forcing a shutdown of the unit.

In addition to the breakage problems, some bundles showed signs of poor membrane formation because tubes within the bundle touched each other and/or the inside of the piping. This phenomenon could also cause false flux and rejection values because membrane imperfections at these places would allow excess flow and poor rejections, even though a good membrane was applied to the rest of the tube. Thus, the tube alignment, size, and bundle-to-piping tolerances are critical to successful membrane formation.

The tube breakage, which caused a number of delays in the pilot plant work, was at first attributed to weak tubes. It was theorized that vibration and pumping pulsations, coupled with the hot alkaline solutions, caused them to break. Also, because most tubes broke at the threaded fitting end, it was also believed that the piping arrangement, which introduced flow at right angles to the bundles at this point, was contributing to excess breakage. The manufacturer performed extensive testing to check these theories and determine whether the ceramic formulation needed adjustment. In these studies the critical harmonic frequencies of tubes were calculated, and extended tests of tube lengths necessary to produce these sympathetic vibrations were performed. Repeated starting and stopping tests were also conducted to determine the effect of high pressure surges on unprotected tubes. In these, as well as in accumulative fatigue tests, no tubes were broken. Bubble point tests of tubes, before and after bundle fabrication, showed that the ceramic formula was within specification. Thus, the ceramic material itself was not at fault.

The breakage of tubes upon loading was traced in part to the piping into which the bundles were inserted. The threaded joints between the module pipes and the tees leaked at high pressure

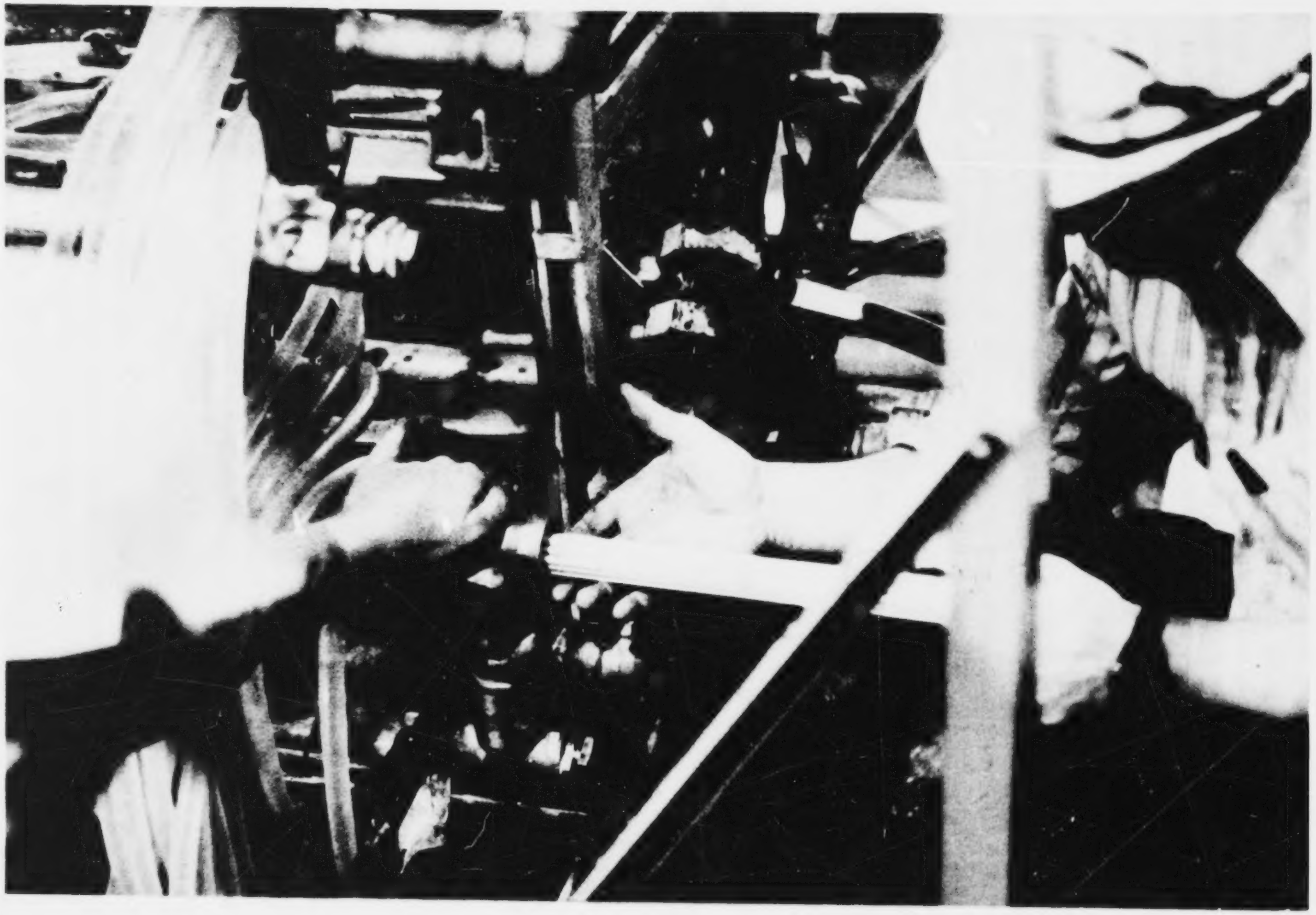


Figure 28. Tube bundle installation: reverse osmosis unit.

and were reinforced with additional welding. This caused a slight swelling of the metal inside the pipe at the point of the weld and also caused the alignment of the tee and the pipe to shift off-center slightly. This problem, plus the handling during shipping and installation, altered the tolerances to the point that the outer tubes rubbed the inside of the piping during installation. This contributed to both breakage and membrane attrition. Imperfections in the bundles also aggravated the problems created by the piping. During the pilot work, it was found that the die for tube formation had worn, causing slightly oversized (by about 0.030 inch) diameter tubes to be made. These bundles could be installed only after several of the outer tubes were removed. Another shipment of bundles contained some which were not aligned perfectly and could not be screwed into the piping. The bundles were used by altering the screw-in plug to a clamp-in arrangement.

It should be noted that these problems have been eliminated in newer systems built by Selas Corporation. The actual configuration is proprietary, but it consists of ceramic tubes which are clamped into a module with beveled seals, removing the necessity of screwing bundles into the module. The concentrate flow is still outside the tubes and with adequate prefiltration, modules of this type have been operated successfully in a pilot installation for over 9000 hours. Thus, the ceramic tube is a viable dynamic membrane support and should not be underrated because of mechanical difficulties experienced while operating a pilot plant designed in the beginning of the development of such systems.

MEMBRANE FORMATION PROCEDURES

Cleaning of Units

The formation of dynamic membranes requires that no contaminants be present in the solution from which the membrane is laid. Extensive preformation cleaning of the wetted surfaces is necessary prior to the membrane formation step. The usual washing procedure for both units involves circulation of basic and acidic solutions at operating pressures and flows through the entire system. The solutions used were 0.5 M NaOH (circulated for several hours) followed by rinses with mill supply water, and 0.5 M HNO_3 (circulated for several hours) followed by repeated rinses with deionized water, until the conductivity of the rinse solution approached that of fresh deionized water. When new tube bundles were installed for a run, this cleaning procedure was performed prior to their installation. When the wash was intended to prepare existing tubes for a new membrane, or was simply intended to improve flux rates, the tubes were washed in place. When a wash was intended for flux improvement only, a solution of Na_2CO_3 has been found to be beneficial, without the problems associated with extremely basic or acidic solutions. The importance of cleaning the units before installing new tube bundles, versus cleaning after installation, was reinforced by the results in Run U-5. In this case, the material being washed off of the piping was apparently deposited on the tubes, adversely affecting the performance of the initial membrane.

Forming the Membranes

Both units use a dual layer membrane that is dynamically formed on the porous ceramic tubes by circulating a solution containing the membrane-forming material over them under pressure and at a surface velocity sufficient to minimize concentration polarization. Both units use the same sublayer material (hydrous zirconium oxide), although it is applied at the pressure peculiar to each unit's operation. The parameters used to determine the progress of the membrane formation are conductivity rejection (% R) as defined earlier and the membrane flux. The flux of new ceramic tubes with no membrane is quite high compared with that of a fully formed membrane, and the conductivity rejection should be zero. By monitoring the rise in % R and the drop in flux and comparing these values to those obtained in laboratory experiments, it is possible to control the formation step. In the pilot plant work it was observed that higher concentrations of the membrane materials in the formation solutions were necessary to form "good" membranes, especially when reforming old membranes, than was predicted from laboratory scale tests. The cause for this is not clear because pilot work with desalination units did not show such aberrations. However, adequate membranes were formed by adding more of these materials (in some cases over eight times the predicted amounts) to the formation solution. This phenomenon was more noticeable with the zirconium oxide layer formation than with either of the secondary layers. Unfortunately, time did not allow a complete study.

Procedure: Reverse Osmosis Unit – –

The unit is washed and filled with deionized water. Sufficient $NaNO_3$ is added to raise the conductivity of the solution to about 5000 μmho/cm (concentration about 0.05 M $NaNO_3$), and the pH is adjusted to 3.9 to 4.2, using NaOH or HNO_3. The pH is critical because this is below the isoelectric point of hydrous zirconium oxide, and the colloidal suspension is least stable in solution at this pH. Hydrous oxide membranes have been found to perform best when formed under these conditions. The unit is started up and this solution is circulated at the normal operating conditions of 6.894×10^6 Pa (1000 psig) and 4.56 m/s (15 ft/sec). The zirconium is added as $Zr(NO_3)_4$ in sufficient quantity to achieve a concentration of about 10^{-4} M. The pH usually must be readjusted upward when the $Zr(NO_3)_4$ is added. This solution is circulated over the tubular supports, with all concentrate and permeate flow being recycled, until the flux drops from its initial high level (usually 8.15 $m^3/m^2/d$ [2000 gfd]) and the salt rejection (measured as conductivity) begins to rise. Ideally, a completed hydrous Zr(IV) oxide membrane should have a conductivity rejection of about 30 to 40% with fluxes of about 1.22 to 2.04 $m^3/m^2/d$ (300–500 gfd). In actual practice, the flux and conductivity rejections occupy much wider ranges. If the membrane performance is not satisfactory, longer formation times or extra $Zr(NO_3)_4$ may be used.

Once the hydrous Zr(IV) oxide membrane is complete, the solution is drained out, and the system is rinsed with deionized water. A fresh $NaNO_3$ solution is then prepared, but the pH is now adjusted to 2.0 to 2.3 using HNO_3. The unit is again started and operated at the usual pressure and flow. The polyacrylic acid (Rohm and Haas Acrysol A–3, molecular weight about 150,000) is added to the tank (about 150 to 180 grams/0.95 m^3 of water) and the unit allowed to run until the flux drops to approximately 5.09 $m^3/m^2/d$ (125 gfd). The pH is then slowly raised in increments of about 0.5 to 1.0 units, allowing the parameters of flux and conductivity rejection to come to a steady state after each adjustment. If the flux does not drop, or if the conductivity rejection is too low, extra polyacrylic acid may be used. In extreme cases, the membrane can be washed off and another formed. Successfully completed membranes should have fluxes of 2.04 to 4.07 $m^3/m^2/d$ (50 to 100 gfd) with conductivity rejections of 88 to 92%. The unit is then rinsed prior to use.

Procedure: Ultrafiltration Unit – –

The system is washed and filled with deionized water. As with the reverse osmosis unit, $NaNO_3$ is added to provide reference conductivity and the pH is adjusted to 3.9 to 4.2 prior to the addition of $Zr(NO_3)_4$ (to obtain a 10^{-4} M solution). The membrane formation is performed at the same velocity, 4.57 m/s (15 ft/sec), but with a higher pressure than that of the usual ultrafiltration operation. The membrane is formed at 2.76×10^6 to 3.10×10^6 Pa (400 to 450 psig), versus the normal operating pressure of 1.59×10^6 Pa (230 psig). The membrane formation step is continued until the flux drops to 8.15 to 16.3 $m^3/m^2/d$ (200 – 400 gfd) and the conductivity rejection increases to about 20 to 30%. If performance is not satisfactory, longer formation times or extra $Zr(NO_3)_4$ can be used. After completion of the hydrous Zr(IV) oxide layer, the solution is drained and the unit rinsed with deionized water. Then another $NaNO_3$ solution is prepared, the unit is started again at an elevated pressure, the pH is adjusted to about 8, and approximately 350 g/0.57 m^3 H_2O of sodium silicate solution (Na_2SiO_3, Matheson, Coleman Bell, 40 – 42° Be) is added. The unit is operated until the flux drops to about 4.07 $m^3/m^2/d$ (100 gfd) and the conductivity rejection increases to 30 to 40%. If these conditions are not reached, additional formation time or extra Na_2SiO_3 may be added. The system is then rinsed prior to use.

SECTION 6

RESULTS

REVERSE OSMOSIS UNIT

The operation of this unit was erratic due to power failures, mechanical problems, and tube bundle breakage. The results given in the following tables and figures must be interpreted in conjunction with the operating times, shutdowns, and subsequent lags in operation. The results of the first successful trial, Run H-1, are shown in Figure 29 and Table 4. This run was limited to eight tube bundles and the membrane formation was abnormal. Excess $Zr(NO_3)_4$ and polyacrylic acid were necessary, and the final fluxes and percent rejection were lower than desired at the end of the formation step. Two bundles showed signs of breakage (high flux and low percent rejection compared with the others) but later approached the same operating levels, as if the membrane had repaired itself. This occurred a number of times during the project and was possibly caused by tube bundle imperfections. The hypothesis is that tube imperfections act as oversized pores that will fill in and become covered with membrane more slowly than the usual tube surfaces.

The unit was started with decker filtrate using no pH adjustment (pH = 10.3) and operated at a pressure of 6.894×10^6 Pa (1000 psig) and a surface velocity of 4.57 m/s (15 ft/sec). The initial flux was 2.44 $m^3/m^2/d$ (60.0 gfd) with a conductivity rejection of 77%. After 12 hours of operation these values had dropped only slightly, and problems with system controls shut down the unit. Because the unit was on and off several times over a span of a few days, the feed tank was drained, refilled with fresh decker filtrate, and restarted on February 9, 1977 (the beginning of Run H-1). Shortly after startup, two of the eight bundles broke and had to be isolated. Excessive pump leakage and power failures stalled the restarting until the next day. Over the next 4 days of operation, the flux dropped from 2.35 to 1.31 $m^3/m^2/d$ (57.6 to 32.2 gfd). The unit was again shut down for a pump repair and restarted on February 15, 1977 with the flux on startup about equal to that before the shutdown. The unit ran for 2 more days until the seals on the feed pump pistons began leaking excessively. This did not cause the unit to shut down, but as concentrate was lost from the pump, raw feed was introduced at a rate higher than permeate production causing undue dilution of the concentrate. The data indicate the rate of concentration of the feed constituents was adversely affected. The run was terminated when the other tube bundles began to break. The bundles were removed and found to contain fiber accumulations.

The reverse osmosis unit was next operated in April, when replacement tube bundles became available. In Run H-2, 29 bundles were loaded, but several were broken during membrane formation and in an initial trial. The broken bundles were removed and found to contain fiber accumulations after only 5 hours of operation. Also, several tubes showed signs of rubbing against the inside of the piping. The unit was started up on May 2, 1977, with a 50 μm rating filter bag placed on the raw feed line. Because the unit had been left dry during the 2-week downtime, the membrane

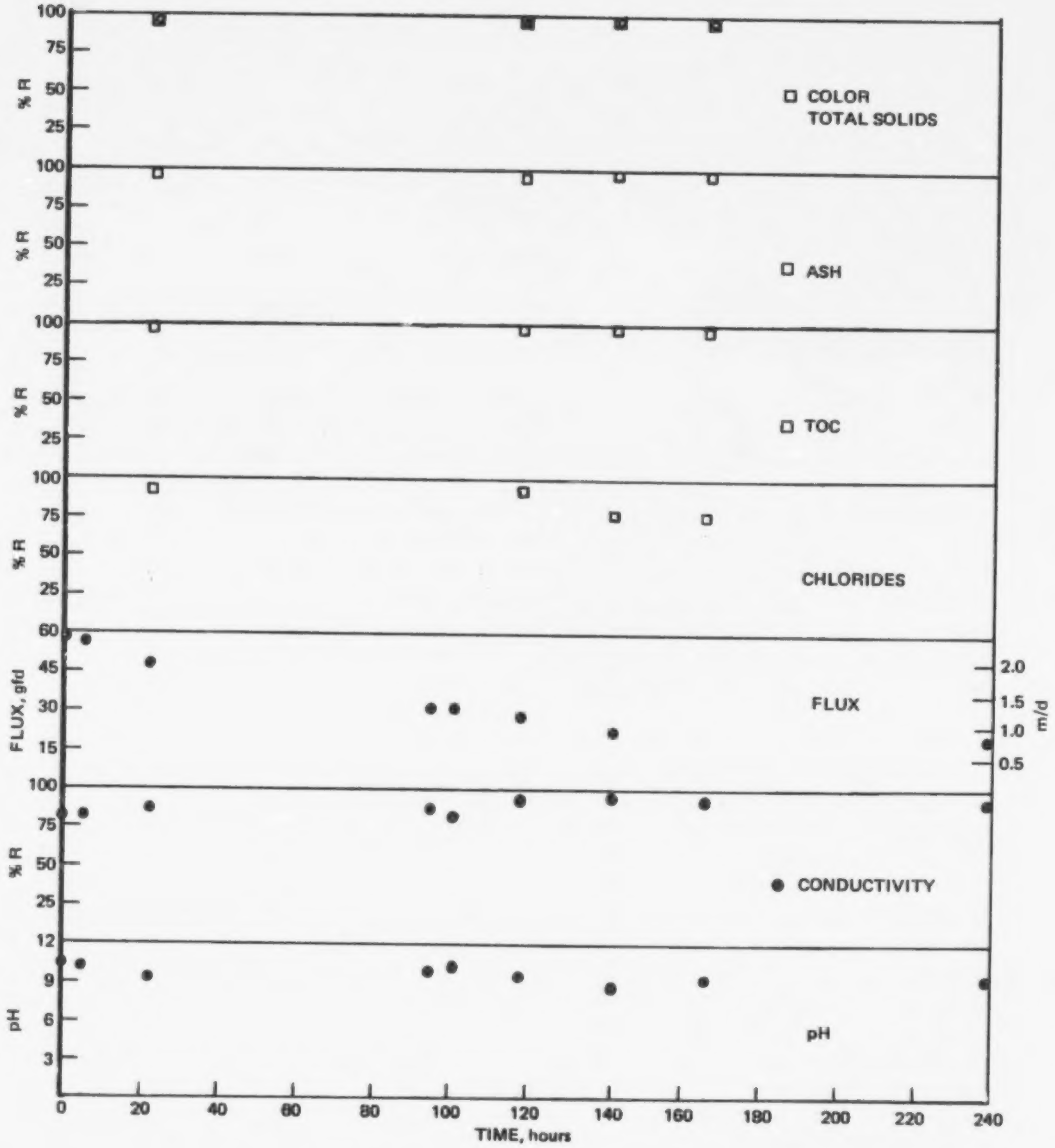


Figure 29. Run H-1. Reverse osmosis of decker filtrate.

6.894×10^6 Pa, 1000 psig	4.57 m/s 15 ft/sec	52°C. pH 8-10

TABLE 4. REVERSE OSMOSIS TREATMENT OF DECKER FILTRATE, RUN H-1

Date, 1977	Elapsed Operating Time, hr.	Flux, $m^3/m^2/d$ (gfd)	pH Concen-trate	pH Per-meate	Conductivity Concen-trate	Conductivity Per-meate	Conductivity % R	Total Solids, p.p.m. Concen-trate	Total Solids, p.p.m. Per-meate	Total Solids, p.p.m. % R	Ash, p.p.m. Concen-trate	Ash, p.p.m. Per-meate	Ash, p.p.m. % R
2-9	1	2.44 (60)	10.0	10.4	530	100.0	81.0	Startup					
10	5[1]	2.35 (57.6)	9.7	10.2	680	110.0	83.8	Restart					
11	22	1.98 (48.7)	9.8	9.3	920	110.0	88.0	457	10.0	97.8	257	9	96.5
14	95	1.31 (32.2)	9.4	9.8	370	57.0	86.2						
15	101[2]	1.27 (31.2)	10.4	10.2	800	140.0	82.5						
16	118	1.19 (29.1)	8.7	9.6	980	70.0	92.8	1444	19.0	98.7	680	17	97.5
17	142	0.92 (22.7)	8.4	8.5	1200	56.0	95.3	1230	4.0	99.6	423	9	99.1
18	166[3]	– –	8.4	9.2	1300	70.0	94.6	1647	12.0	99.3	572	6	99.0
21	238	0.81 (19.8)	8.3	9.5	1400	88.0	93.7	–	–	–	–	–	–

(continued)

Date, 1977	Elapsed Operating Time, hr.	Volatile Solids, p.p.m. Concen-trate	Volatile Solids, p.p.m. Per-meate	Volatile Solids, p.p.m. % R	Color, c.u. Concen-trate	Color, c.u. Per-meate	Color, c.u. % R	Chlorides Concen-trate	Chlorides Per-meate	Chlorides % R
2-9	1									
10	5[1]									
11	22	200	1	99.5	2440	0	100.0	42	3	92.9
14	95									
15	101[2]									
16	118	764	2	99.7	3720	0	100.0	28	2	92.9
17	142	807	0	100.0	3160	2.5	99.9	24	5	79.2
18	166[3]	1075	6	99.4	4000	0	100.0	24	5	79.2
21	238	–	–	–	–	–	–	–	–	–

[1] Unit down for power failure and repair. Restarted 2/10/77.

[2] Unit down to repair pump. Restarted 2/15/77.

[3] Found pump piston seals leaking excessively. Concentrate in tank diluted by excess raw feed.

performance may have been altered. The initial flux was 3.52 $m^3/m^2/d$ (86.4 gfd) and the flux on startup on May 2, 1977 was 3.30 $m^3/m^2/d$ (81.0 gfd). The flux dropped to 1.53 $m^3/m^2/d$ (37.6 gfd) within 18 hours and declined to 0.46 $m^3/m^2/d$ (11.3 gfd) within 97 hours. At this time, the power to the unit was shut off and did not become available again until May 10, 1977. Mechanical problems delayed startup until May 11, 1977, and the membrane initially showed no significant difference in performance as a result of the delay. The next day the tube bundles started breaking, the flux was low, and extreme pressure fluctuations occurred. The unit was shut down and rinsed the next day which resulted in more tube breakage. A subsequent wash with a Na_2CO_3 solution (pH = 10.6) produced a slight improvement in flux and the loss of more tube bundles. An attempt at restarting with fresh decker filtrate resulted in a flux of 1.80 $m^3/m^2/d$ (44.1 gfd), but a power failure and the following restart broke all but three of the remaining tube bundles. On shutting down the unit and removing the broken tubes, it was discovered that fibers had again collected in the tube bundles and that biological activity was producing a slime layer and swelling up the fiber mats, producing a stress on the tubes. It was later found that the fibers had gotten into the system when the filter bag clogged up during a high fiber load period and that raw decker filtrate had overflowed into the tank. The data for Run H-2 are summarized in Figure 30 and Table 5.

During a wash sequence to prepare the unit for another trial, the surge dampener on the pump outlet sprang a leak. On disassembling the unit, the dampener was found to be irreparably damaged by corrosion. A replacement surge dampener was ordered from Eaton Corporation and was installed in early September. The unit was loaded with tube bundles and a NaOH wash was performed. The hydrous Zirconium oxide membrane was formed using an excess of $Zr(NO_3)_4$, and this resulted in a lower than desirable flux and percentage of rejection. There were several power failures during the polyacrylic acid (PAA) membrane formation. The solution being circulated formed a black precipitate as the NaOH was added to raise the pH, indicating that iron was probably being dissolved from the surge dampener. The flux was initially 5.5 $m^3/m^2/d$ (135.3 gfd) before the PAA was added, rose during the formation step, and dropped to a final level of 3.39 $m^3/m^2/d$ (83.2 gfd) with a conductivity rejection of only 8.75% (at pH = 8.65). It appeared that the dissolved iron had coagulated the PAA, because the solution contained clumps of brownish-black material which were not present in previous trials.

This membrane's low rejection at a fairly high flux indicated a poor formation, so the unit was washed out with a NaOH solution (pH = 12). Then another PAA formation step was attempted, with emphasis on minimizing the exposure of the carbon steel surge dampener to the low pH (pH = 2) solution. This formation step followed the same pattern as the preceding one, with a final flux of 5.04 $m^3/m^2/d$ (123.6 gfd) and a conductivity rejection of only 20.8%, again indicating a poor membrane. The surge dampener was removed, cleaned, and coated (wetted parts) with an epoxy-base paint to prevent corrosion. The surge dampener was reinstalled and several of the broken tube bundles removed. The signs of wear on the sides of the bundles indicated that the tubes had been rubbing the piping, contributing to poor membrane formation.

The formation of the PAA membrane was completed, with a final flux of 4.38 $m^3/m^2/d$ (107.6 gfd) and a low conductivity rejection of 28%, indicating that the membrane was still not optimal. It was decided to try to use this membrane, because the rubbing tubes might have made it impossible to form a better one. Run H-3, summarized in Figure 31 and Table 6, began on October 28, 1977 using fresh decker filtrate filtered through a 10 μm rating filter bag. The unit achieved a flux of 4.12 $m^3/m^2/d$ (101.1 gfd) on startup, giving a brown initial filtrate which cleared up in about 15 minutes. The conductivity rejection was then 89.3%, at a flux of 3.72 $m^3/m^2/d$ (91.3 gfd). The

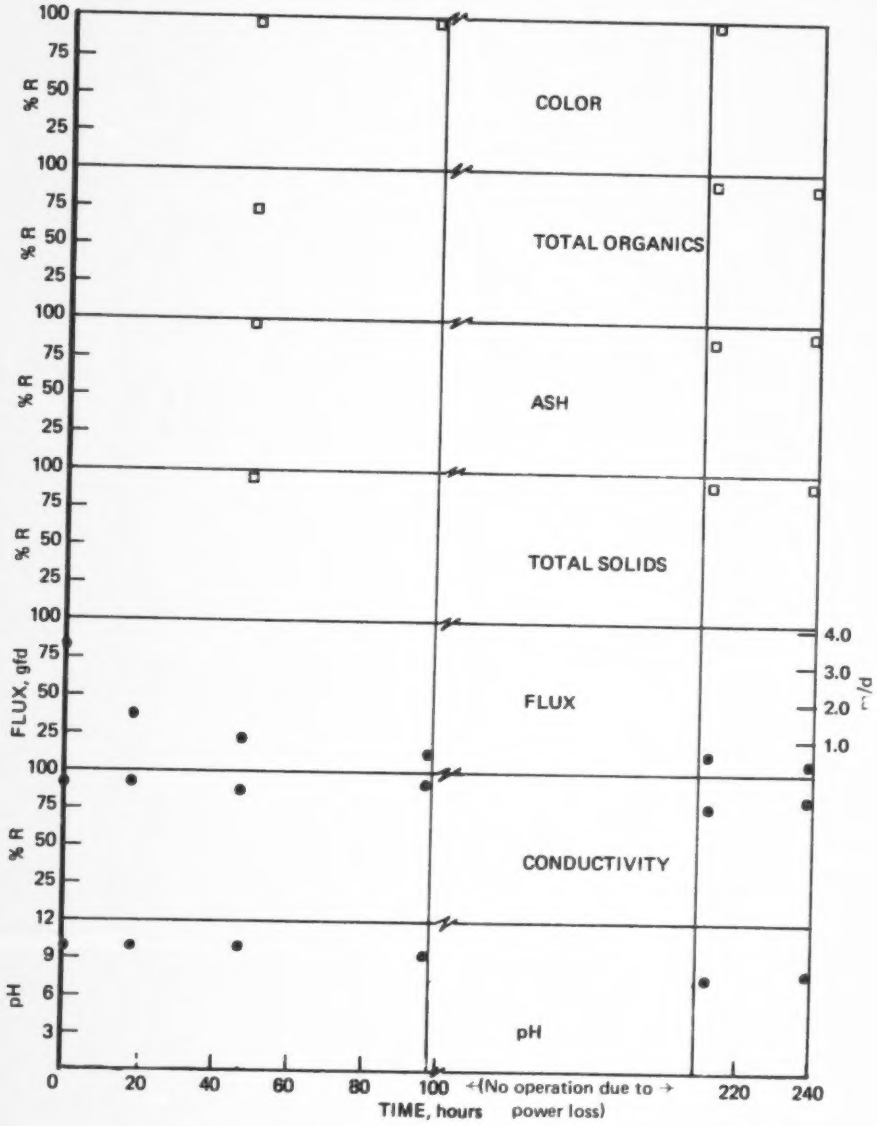


Figure 30. Run H-2. Reverse osmosis treatment of decker filtrate.

6.894×10^6 Pa
1000 psig

4.57 m/s
15 ft/sec

52°C.
pH 8-10

(ACTUAL ELAPSED OPERATING TIME 126 HOURS.)

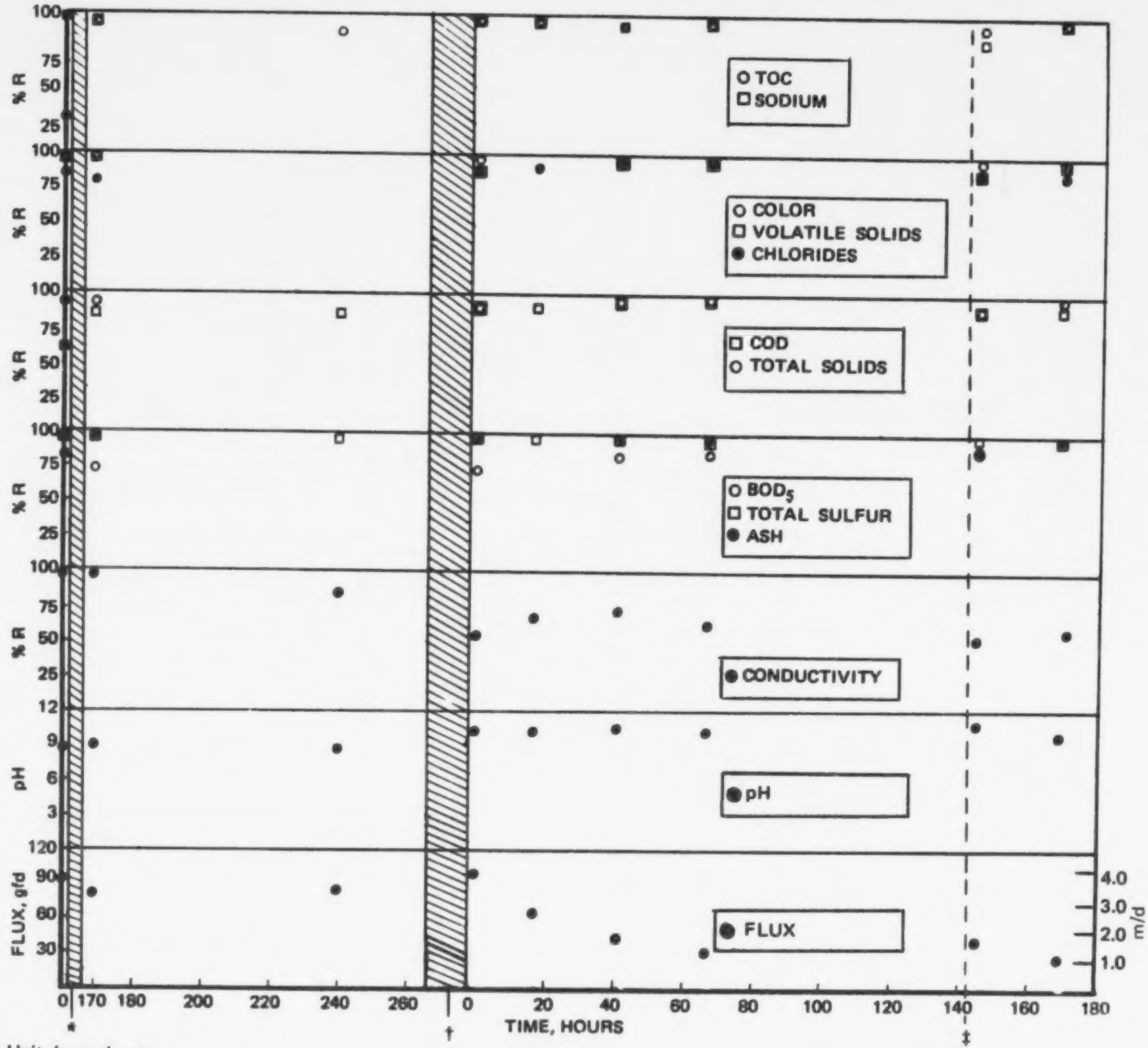
TABLE 5. REVERSE OSMOSIS TREATMENT OF DECKER FILTRATE, RUN H-2

Date, 1977	Elapsed Operating Time, hr.	Flux, $m^3/m^2/d$ (gfd)	pH		Conductivity			Total Solids, p.p.m.		
			Concentrate	Permeate	Concentrate	Permeate	% R	Concentrate	Permeate	% R
5-2	1	3.30 (81.0)	9.9	9.9	1100	130	88.2	Startup		
3	18	1.53 (37.6)	9.9	9.9	2200	260	88.0			
4	47	0.82 (20.2)	10.1	9.7	3200	420	86.9	5579	278	95.0
6	97[1]	0.46 (11.3)	9.7	9.4	3200	380	88.1	5938	–	–
11	103	0.51 (12.5)	7.7	7.4	2600	600	76.9	4615	408	91.2
12	126	0.37 (9.1)	8.1	7.8	2700	490	81.9	4758	387	91.9

(continued)

Date, 1977	Elapsed Operating Time, hr.	Ash, p.p.m.			Volatile Solids, p.p.m.			Color, c.u.		
		Concentrate	Permeate	% R	Concentrate	Permeate	% R	Concentrate	Permeate	% R
5-2	1	Startup								
3	18									
4	47	1810	64	96.5	3769	214	94.3	19,600	45	99.8
6	97[1]	1961	–	–	3977	–	–	18,400	45	99.8
11	103	1527	170	89.9	3088	238	92.3	19,600	250	98.7
12	126	1815	111	93.9	2943	276	90.6	21,800	480	97.8

[1] Shut down due to power failure.



* Unit down due to mechanical problems

† Unit down to install new tubes and membrane

‡ Membrane washed

Figure 31. Run H-3. Reverse osmosis treatment of decker filtrate.

6.894×10^6 Pa
1000 psig

4.57 m/s
15 ft/sec

52°C
pH 8-11

(ACTUAL ELAPSED OPERATING TIME BEFORE MEMBRANE REPLACEMENT 37 HOURS.)

TABLE 6. REVERSE OSMOSIS TREATMENT OF DECKER FILTRATE, RUN H-3

Date, 1977	Elapsed Operating Time, hr.	Flux, $m^3/m^2/d$ (gfd)	pH Concentrate	pH Permeate	Conductivity Concentrate	Conductivity Permeate	Conductivity % R	Total Solids, p.p.m. Concentrate	Total Solids, p.p.m. Permeate	Total Solids, p.p.m. % R	Ash, p.p.m. Concentrate	Ash, p.p.m. Permeate	Ash, p.p.m. % R	Chloride, p.p.m. Concentrate	Chloride, p.p.m. Permeate	Chloride, p.p.m. % R
10/28	7	3.72 (91.3)	9.65	8.95	1400	150	89.3	1389	77	94.5	527	32	93.9	24.6	3.4	86.2
11/4	1[1]	3.18 (78.1)	9.05	9.00	1100	92	91.6	884	57	93.6	373	10	97.3	25.3	4.1	83.8
11/7	6[2]	3.42 (84.0)	8.80	8.70	1400	200	85.7	—	—	—	—	—	—	—	—	—
11/8	30	5.05 (124.0)	—	—	—	—	—	—	—	—	—	—	—	—	—	—
11/22	0.5[3]	3.95 (97.0)	10.00	10.20	1200	530	55.8	884	70	92.1	359	4	98.9	30.7	3.5	88.6
11/23	17	2.73 (67.0)	9.90	10.20	1500	500	66.7	—	—	—	—	—	—	37.2	3.1	91.7
11/24	41	1.86 (45.6)	10.00	10.40	2100	600	71.4	2668	101	96.2	1034	40	96.1	55.9	4.9	91.2
11/25	67	1.40 (34.4)	9.70	10.20	1600	600	62.5	2648	96	96.2	940	45	95.2	59.1	6.4	89.2
11/28	145[4]	1.74 (42.8)	10.45	10.80	1650	800	51.5	2076	234	88.7	777	104	86.6	53.6	8.3	84.5
11/29	169	1.09 (26.7)	9.20	9.75	1150	500	56.5	1415	40	97.2	460	18	96.1	29.7	3.3	88.9

(continued)

Date, 1977	Elapsed Operating Time, hr.	Flux, $m^3/m^2/d$ (gfd)	Color, c.u. Concentrate	Color, c.u. Permeate	Color, c.u. % R	Sodium, p.p.m., as Na Concentrate	Sodium, p.p.m., as Na Permeate	Sodium, p.p.m., as Na % R	5-Day BOD, p.p.m. Concentrate	5-Day BOD, p.p.m. Permeate	5-Day BOD, p.p.m. % R	COD, p.p.m. Concentrate	COD, p.p.m. Permeate	COD, p.p.m. % R
10/28	7	3.72 (91.3)	4575	27	99.4	177.0	0.5	99.7	430	66	84.7	1450	575	60.3
11/4	1[1]	3.18 (78.2)	1700	15	99.1	108.0	10.0	90.7	210	58	72.4	780	96	87.7
11/7	6[2]	3.42 (84.0)	—	—	—	—	—	—	—	—	—	—	—	—
11/8	30	5.05 (124.0)	—	—	—	—	—	—	—	—	—	—	—	—
11/22	0.5[3]	3.95 (97.0)	2230	0	100.0	143	2.6	98.2	220	58	73.6	620	69	88.9
11/23	17	2.73 (67.0)	—	—	—	200.4	11.1	94.5	—	—	—	1389	104	92.5
11/24	41	1.86 (45.6)	6850	0	100.0	431.0	25.1	94.2	440	87	80.2	2034	135	93.4
11/25	67	1.40 (34.4)	8050	19	99.8	385.2	21.2	94.5	440	64	85.5	2679	129	95.2
11/28	145[4]	1.74 (42.8)	7200	78	98.9	319.7	54.7	82.9	480	45	90.6	2728	161	94.1
11/29	169	1.09 (26.7)	4250	75	98.2	128.6	3.3	97.4	—	—	—	1468	88	94.0

(continued)

Date, 1977	Elapsed Operating Time, hr.	Flux, $m^3/m^2/d$ (gfd)	TOC, p.p.m. Concentrate	TOC, p.p.m. Permeate	TOC, p.p.m. % R	Total Sulfur, p.p.m. Concentrate	Total Sulfur, p.p.m. Permeate	Total Sulfur, p.p.m. % R	Volatile Solids, p.p.m. Concentrate	Volatile Solids, p.p.m. Permeate	Volatile Solids, p.p.m. % R
10/28	7	3.72 (91.3)	54	40.3	25.4	42.5	1.6	96.2	862	45	94.8
11/4	1[1]	3.18 (78.2)	340	30.5	91.0	41.3	1.7	95.9	511	26	94.9
11/7	6[2]	3.42 (84.0)	480	53.7	88.8	67.0	3.3	95.1	—	—	—
11/8	30	5.05 (124.0)	—	—	—	—	—	—	—	—	—
11/22	0.5[3]	3.95 (97.0)	334	27.9	91.6	33.0	1.0	97.0	525	66	87.4
11/23	17	2.73 (67.0)	495	30.0	93.9	42.0	1.0	97.6	—	—	—
11/24	41	1.86 (45.6)	807	47.0	94.2	87.0	1.3	98.6	1634	61	96.3
11/25	67	1.40 (34.4)	812	40.0	95.1	83.0	8.2	90.1	1608	51	96.8
11/28	145[4]	1.74 (42.8)	666	47.4	92.9	70.0	2.4	96.6	1299	130	90.0
11/29	169	1.09 (26.7)	474	29.2	93.8	42.5	1.0	97.6	955	28	97.1

[1] Mechanical problems 10/31/77. Restarted with fresh feed 11/4/77.

[2] Unit shut down over the weekend.

[3] Unit restarted with new tubes and membrane.

[4] Unit down. Cleaned membrane; restarted with fresh decker filtrate

unit was found shut down on October 31, 1977 because of a malfunctioning feed valve. The valve was replaced, the unit flushed, and restarted with fresh decker filtrate on November 4, 1977. The flux was 3.18 $m^3/m^2/d$ (78.2 gfd) with a conductivity rejection of 91.6, and the unit was shut down over the weekend, rather than risk an accidental shutdown.

The unit was restarted on November 7, 1977 with only 10 unbroken bundles left, obtaining a flux of 3.42 $m^3/m^2/d$ (84.0 gfd) and a conductivity rejection of 85.7%. The flux was higher the next day, but more bundles were broken. The unit was shut down when a high pressure cutoff turned off the pump. An attempt to restart it caused the safety rupture disk to blow out and shut down the unit again. On removing the tube bundles, it was found that broken pieces of tubes had jammed the piping and blocked the flow after only 30 hours of operation. Fibers were again caught in the tube bundles, and a build up of pitch was noticed. The unit was cleaned out and the 9 available bundles installed. A new membrane was formed, and the unit restarted on November 22, 1977.

The new membrane obtained a flux of 3.95 $m^3/m^2/d$ (97.0 gfd) with a conductivity rejection of 54.2%. The unit ran until the morning of November 28, 1977, when it was found down with the filter bag overflowing into the tank. The unit was drained and flushed with water and a NaOH solution (pH = 11.9). The unit was restarted with fresh decker filtrate, achieving a flux of 1.74 $m^3/m^2/d$ (42.8 gfd) and a conductivity rejection of 51.5%. The unit shut down again on November 29, 1977 because of several broken bundles. It was restarted with one bundle left giving a flux of 1.09 $m^3/m^2/d$ (26.7 gfd), with the pressure drop through the unit increasing, indicating a progressive blockage. On November 30, 1977, it was found shut down with a blown rupture disk. The reverse osmosis portion of this project was then terminated.

ULTRAFILTRATION UNIT

The operation of the ultrafiltration unit was also erratic because of power and equipment failures. The data presented in the following graphs and tables must be interpreted along with the fact that these repeated shutdowns prevented the unit from reaching any semblance of a steady state. The unit first ran in September of 1976, but mechanical problems prevented the gathering of much useful data. A Zr(IV)–Si(IV) oxide membrane was formed, giving a flux of 2.93 $m^3/m^2/d$ (72 gfd) and a conductivity rejection of only 19%. This membrane was subsequently covered with another complete dual-layer membrane in an attempt to improve upon performance. These parameters did not improve, so the system was started on September 23, 1976 with fresh caustic extract (E_1) using only nine bundles (the others had broken). The initial flux was 2.16 $m^3/m^2/d$ (26.6 gfd) in 2 days. On September 26, 1976, the pH control system malfunctioned, causing the tank to overflow. The flux at this time was only 0.19 $m^3/m^2/d$ (4.6 gfd), so the unit was rinsed with water and a Na_2CO_3 solution. During the rinse sequence September 28, 1976, a pump bearing failed and had to be replaced. The pump was repaired on October 12, 1976, and caustic (1 $\underline{M}$ NaOH) and acidic (1 $\underline{M}$ HNO_3) washes were performed. Then another membrane was applied, with 15 bundles in operation. During this formation step the pump was irreparably damaged, and the unit was left full of deionized water until a replacement pump arrived.

On February 2, 1977, the system was again operable, and fresh E_1 was added to the tank. No pH control was used in this or subsequent runs. The unit was started up for a short time on February 2, 1977 and achieved a flux of 2.30 $m^3/m^2/d$ (56.6 gfd). Over the next few days, the unit was operated intermittently as control and other mechanical problems were corrected.

The flux gradually rose to 4.72 $m^3/m^2/d$ (115.9 gfd) as the unit was operated. On February 11, 1977, the unit was filled with fresh E_1, and Run U-1 began. The flux dropped from an initial value of 5.13 $m^3/m^2/d$ (126 gfd) to 3.58 $m^3/m^2/d$ (87.7 gfd) on February 14, 1977. The unit was shut down on February 15, 1977 because of controller malfunction, and when it was restarted it produced a flux of 3.28 $m^3/m^2/d$ (80.5 gfd). The flux held fairly steady for the rest of this run, in the range of 3.67 to 4.56 $m^3/m^2/d$ (90 to 112 gfd), until the last few days of operation when the total solids content of the concentrate stream rose above 10% (see Figure 32 and Table 7). The data from February 18, 1977 to February 28, 1977 are not representative of the unit's capabilities because the unit was not operating for several days during this period, and at one time the feed control valve jammed open, diluting the concentrate. The unit restarted on February 28, 1977. The rejections of color, total solids, volatile solids, and ash were high throughout the run. The flux dropped when solids content in the concentrate stream was increased (see Figure 33 and Table 8) as expected. However, the pressure drop through the unit did not increase significantly when solids concentration was increased (see Figure 34 and Table 9).

The unit's operation after March 10, 1977 was too irregular to generate useful data because of numerous mill power failures. The tank was refilled with fresh waste water (E_1) and restarted on March 15, 1977, achieving a flux of 3.74 $m^3/m^2/d$ (91.8 gfd) on March 16, 1977 after approximately 12 hours of operation. The flux dropped to 3.10 $m^3/m^2/d$ (71.1 gfd) 3 days later and a water rinse was performed. The unit was restarted with fresh waste water (E_1) and was giving a flux of 6.36 $m^3/m^2/d$ (156.1 gfd) after 1.5 days. The operation of the unit was again irregular for the next 5 days because of mechanical problems in the bleach plant, but each time the unit was restarted the flux was greater than 4.48 $m^3/m^2/d$ (110 gfd). Soon after this, tube bundles began to break, and the unit was shut down to remove them. The bundles were found to be clogged with pulp fibers. These fibers not only contributed to bundle breakage but drastically altered flow conditions in and around the tubes. Unfortunately, no chemical data are available for the operation after Run U-1. However, the effect of the water rinse on the flux is significant.

At this time no ceramic tube bundles were available, so the UCARSEP™ carbon tube module supplied by the Union Carbide Corporation was installed. This module could not be used in conjunction with the ceramic tubes because it had a pressure limit of 8.62 x 10^5 Pa (125 psig). The unit was supplied with a proprietary membrane already applied, and it had been stored full of water until this time. Prior to startup with the waste water (E_1), the module was rinsed with mill supply water. During this rinse, the rinse water stream turned brown for a short time, as if dark suspended solids were being flushed out of the module. The unit was then started up with fresh waste water (E_1) at an inlet pressure of 7.93 x 10^5 Pa (115 psig). The permeate was initially a dark brown and after an hour of operation, it was still as dark as the feed with a conductivity rejection of 2.3%. It was concluded that the membrane material had loosened from the support during the storage period and had sloughed off on startup. The UCARSEP™ module was not used further because ceramic tube bundles were due to arrive shortly.

The newer tubes were fabricated into bundles by Oak Ridge National Laboratory personnel and installed on April 25, 1977. Then a membrane (Zr[IV]-Si[III] oxide) was formed. Several bundles were broken during the formation step. On removal it was found that the epoxy cement used to join the bundles to the steel fitting had failed and allowed one entire bundle to slide into another, damaging both. Another problem was that these tubes were slightly larger in diameter than the previous ones, and the tubes which were removed showed signs of rubbing the piping. This observation becomes more important when considered in conjunction with the fact that the

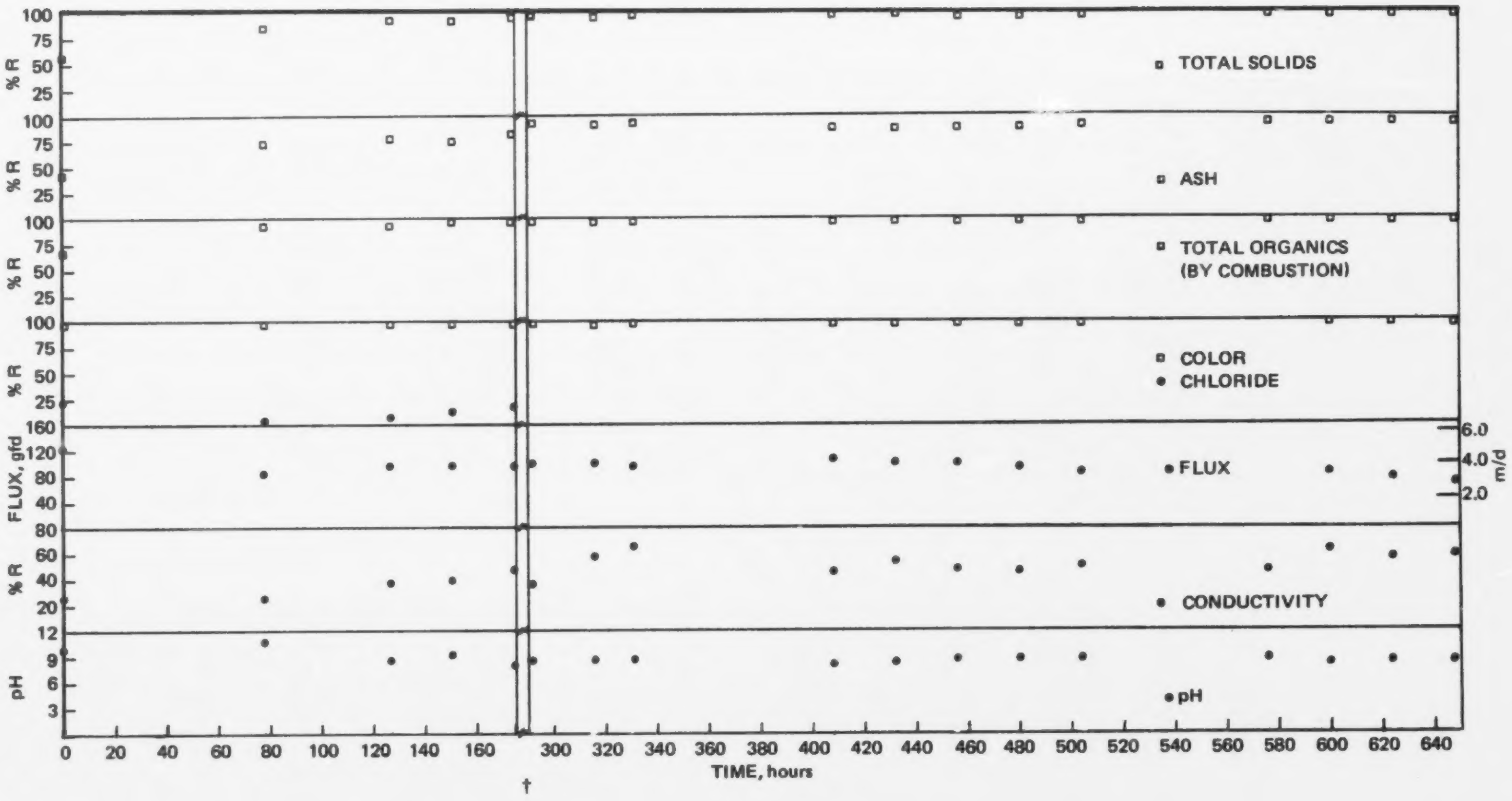


Figure 32. Run U-1. Ultrafiltration of caustic bleach effluent (E$_1$).

1.65 x 10^{6}Pa	4.57 m/s	pH 8-10
240 psig	15 ft/sec	52°C

(ACTUAL ELAPSED OPERATING TIME 470 HOURS)

†UNIT DOWN FOR CONTROLLER REPAIR.

TABLE 7. ULTRAFILTRATION OF CAUSTIC BLEACH PLANT EFFLUENT, RUN U-1

Date, 1977	Elapsed Operating Time, hr.	Flux, $m^3/m^2/d$ (gfd)	pH		Conductivity			Total Solids, p.p.m.		
			Concentrate	Permeate	Concentrate	Permeate	% R	Concentrate	Permeate	% R
2-11	3	5.13 (126.0)	10.3	10.2	5000	3700	26.0	8555	3761	56.0
14	68	3.58 (87.8)	10.6	10.8	5500	4000	27.3	24,804	3513	85.8
16	90[1]	3.93 (96.6)	8.6	8.6	4800	2900	39.6	37,505	2926	92.2
17	115	3.93 (96.6)	9.2	9.3	5000	3000	40.0	38,340	2764	92.8
18	139	3.93 (96.6)	8.2	8.2	5000	2600	48.0	48,941	2184	95.5
23	172[2]	4.22 (103.5)	8.5	8.5	4100	1500	36.6	49,730	1605	96.8
24	196	4.22 (103.5)	8.2	8.5	4900	2000	59.2	45,981	1886	95.9
25	206	3.93 (96.6)	8.4	8.7	4300	1400	67.4	57,152	1304	97.7
—	Unit down over weekend									
28	230	4.54 (111.5)	8.0	8.3	4600	2400	47.8	60,461	2214	96.0
3-1	254	4.22 (103.5)	8.0	8.4	5500	2500	54.5	68,193	2252	96.7
2	278	4.07 (100.0)	8.8	8.9	5800	3000	48.3	68,449	2789	95.9
3	302	3.81 (93.5)	8.3	8.7	6000	3200	46.6	75,640	2864	96.2
4	326	3.48 (85.3)	8.4	8.7	6200	3000	51.6	87,929	2683	96.9
7	398	— —	7.9	8.6	6500	2500	61.5	96,592	2374	97.4
8	422	3.48 (85.3)	8.1	8.3	6200	2300	62.9	97,116	2360	97.6
9	446	3.11 (76.3)	8.0	8.4	6400	2800	56.3	113,045	3285	97.1
10	470	2.68 (65.9)	8.0	8.4	6400	2700	57.8	122,945	3189	97.4

(continued)

Date, 1977	Elapsed Operating Time, hr.	Flux, $m^3/m^2/d$ (gfd)	Ash, p.p.m.			Volatile Solids, p.p.m.			Color, c. u.		
			Concentrate	Permeate	% R	Concentrate	Permeate	% R	Concentrate	Permeate	% R
2-11	3	5.13 (126.0)	3800	2202	42.1	4755	1559	67.2	28,500	326	98.9
14	68	3.58 (87.8)	8504	2220	73.9	16,300	1293	92.1	162,500	1260	99.2
16	90[1]	3.93 (96.6)	5729	1320	77.0	31,776	1606	94.9	250,000	1800	99.3
17	115	3.93 (96.6)	5931	1460	75.4	32,409	1304	96.0	287,500	1848	99.4
18	139	3.93 (96.6)	8838	1232	86.1	40,103	952	97.6	345,000	2030	99.4
23	172[2]	4.22 (103.5)	8857	568	93.6	40,873	1037	97.5	325,000	1700	99.5
24	196	4.22 (103.5)	9636	835	91.3	36,345	1051	97.1	385,000	2050	99.5
25	206	3.93 (96.6)	9861	580	94.1	47,291	724	98.5	390,000	1350	99.7
—	Unit down over weekend										
28	230	4.54 (111.5)	10,874	1130	89.6	49,587	1084	97.8	500,000	2200	99.6
3-1	254	4.22 (103.5)	12,411	1422	88.5	55,782	830	98.5	554,000	3100	99.4
2	278	4.07 (100.0)	14,799	1822	87.7	53,650	967	98.2	560,000	3450	99.4
3	302	3.81 (93.5)	15,437	1871	89.9	60,203	993	98.4	476,000	4050	99.3
4	326	3.48 (85.3)	16,435	1602	90.3	71,494	1081	98.5	614,000	4120	99.3
7	398	— —	18,086	1319	92.7	78,496	1055	98.7	645,000	3300	99.5
8	422	3.48 (85.3)	17,311	1120	93.5	79,805	1240	98.4	680,000	4400	99.4
9	446	3.11 (76.3)	18,796	1595	91.5	94,249	1690	98.2	850,000	4550	99.5
10	470	2.68 (65.9)	18,313	1585	91.3	104,632	1604	98.7	890,000	4600	99.5

[1] Unit down 2/15/77. Restarted.

[2] Unit down 2/19/77. Restarted.

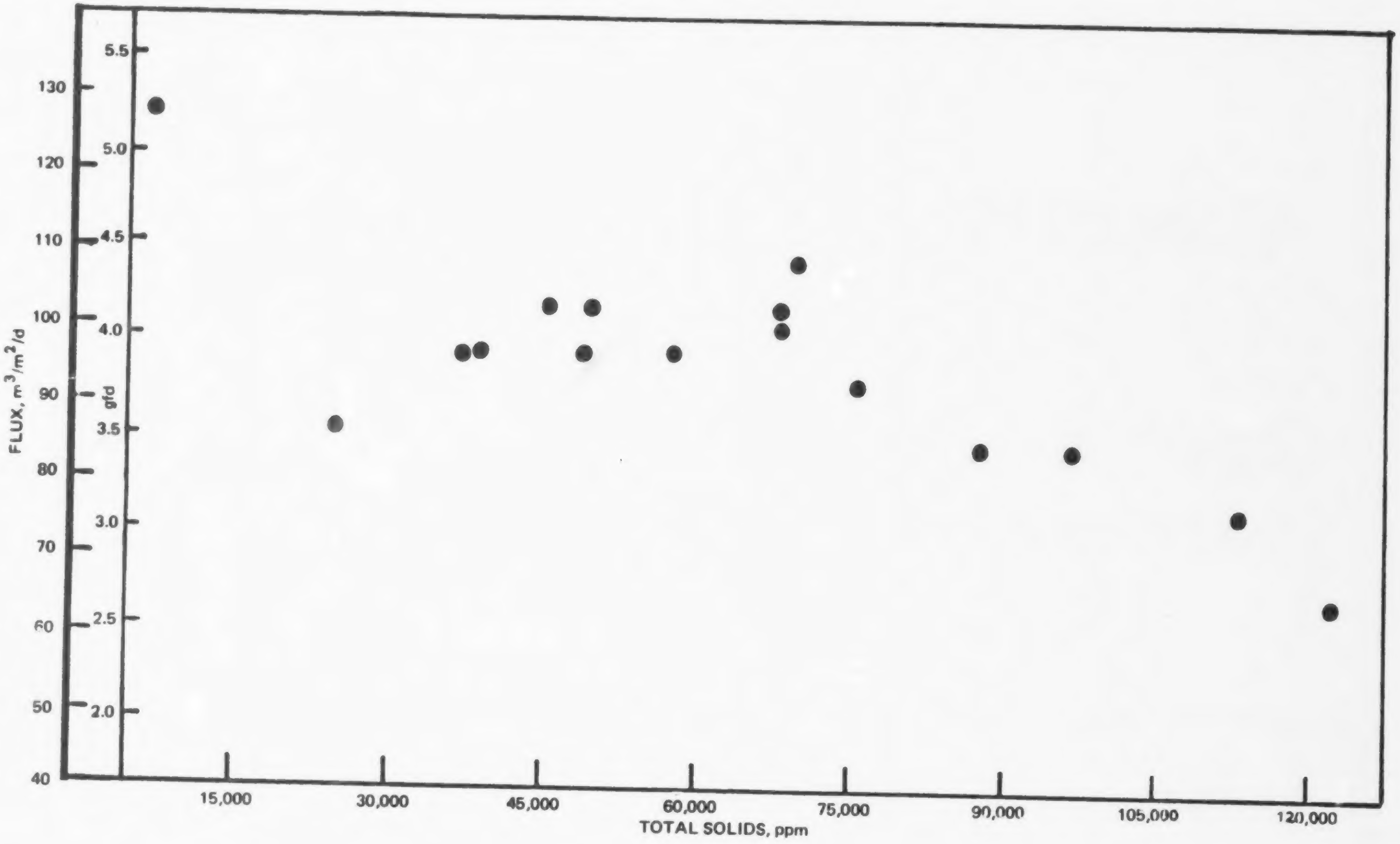


Figure 33. Flux vs. total solids in concentrate, Run U-1.

TABLE 8. FLUX VS. CONCENTRATE SOLIDS CONCENTRATION, RUN U-1

Date, 1977	Flux $m^3/m^2/d$	Flux (gfd)	Total Solids, p.p.m.
2-11	5.13	(126.0)	8555
14	3.56	(87.8)	24,804
16	3.94	(96.6)	37,505
17	3.94	(96.6)	38,340
18	3.94	(96.6)	48,941
23	4.22	(103.5)	49,730
24	4.22	(103.5)	45,981
25	3.94	(96.6)	57,152
28	4.54	(111.5)	69,461
3-1	4.22	(103.5)	68,193
2	4.07	(100.0)	68,449
3	3.81	(93.5)	75,640
4	3.48	(85.3)	87,929
7	–	–	96,592
8	3.48	(85.3)	97,116
9	3.11	(76.3)	113,045
10	2.68	(65.9)	122,945

TABLE 9. PRESSURE DROP VS. CONCENTRATE SOLIDS CONCENTRATION, RUN U-1

Date, 1977	Pressure Drop, Pa (psig)	Total Solids, p.p.m.
2-11	9.65×10^5 (140)	8553
14	1.03×10^6 (150)	24,804
15	1.07×10^6 (155)	–
16	1.10×10^6 (160)	37,505
17	1.21×10^6 (175)	38,340
18	1.21×10^6 (175)	48,941
23	1.21×10^6 (175)	49,730
24	1.24×10^6 (180)	45,981
25	1.24×10^6 (180)	57,152
28	1.24×10^6 (180)	60,461
3-1	1.21×10^6 (175)	68,193
2	1.21×10^6 (175)	68,449
3	1.17×10^6 (170)	75,640
4	1.17×10^6 (170)	87,929
7	1.24×10^6 (180)	96,592
8	1.17×10^6 (170)	97,116
9	1.17×10^6 (170)	113,045
10	1.17×10^6 (170)	122,945

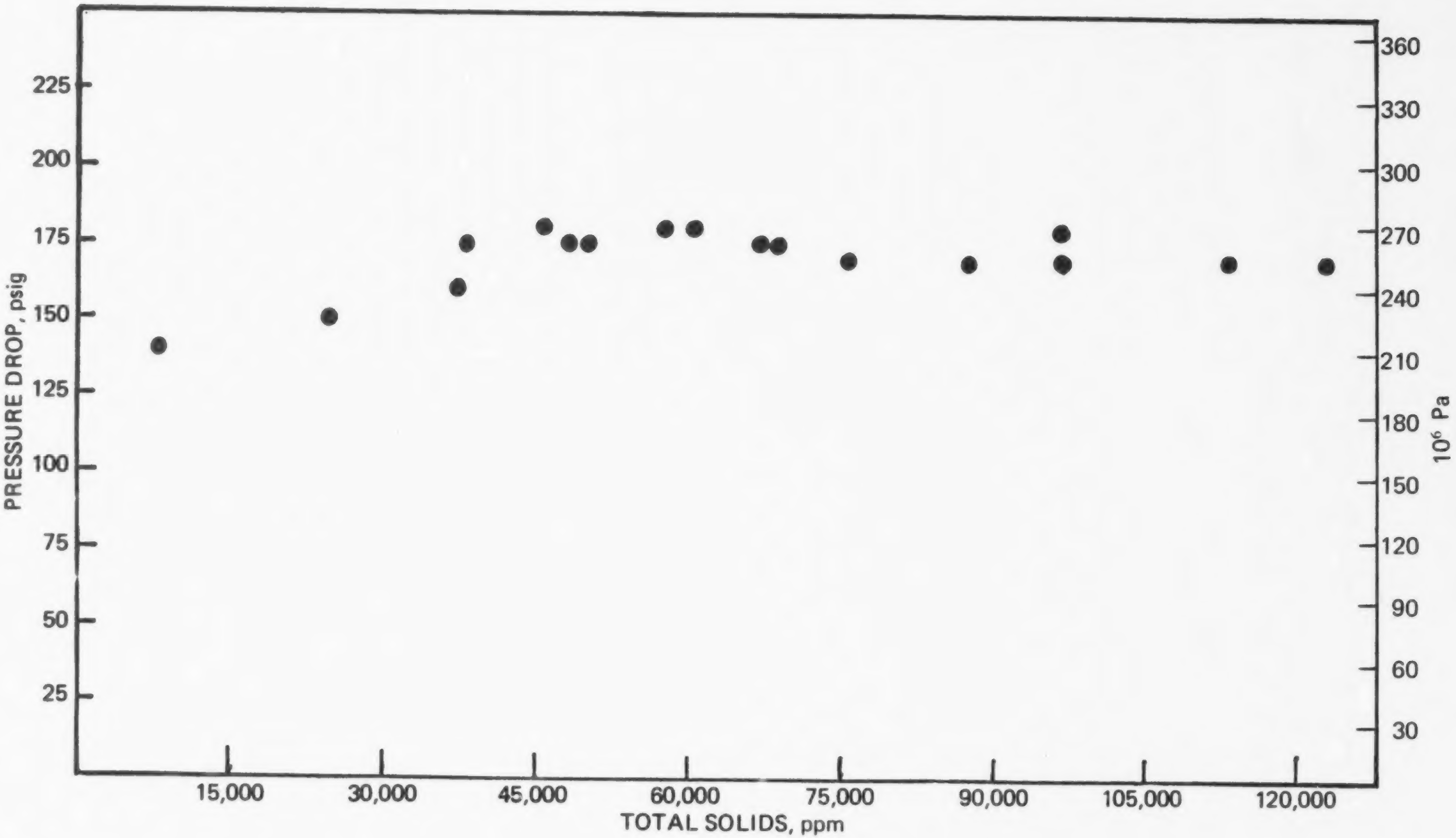


Figure 34. Pressure drop vs. total solids concentration, Run U-1.

membrane, when formed, gave lower rejections (13.5% conductivity) than desired at the end of the formation step. This was possibly caused by the membrane having a thin spot at the point of contact. The high flux through spots could cause the operator to apply excess material and form a thicker than necessary membrane (with lower flux) over the bulk of the tubes, while the high flux and poor rejection indicates that membrane formation should continue.

It was decided to try this membrane with the waste water (E_1) despite the fact that its quality was less than desired. A 10 μm rating filter bag was used to filter the raw feed. The initial flux was 2.43 $m^3/m^2/d$ (59.7 gfd) with a 31.6% conductivity rejection, but the permeate was not clear. The flux dropped to 1.58 $m^3/m^2/d$ (38.9 gfd) within 30 minutes and to 1.35 $m^3/m^2/d$ (33.2 gfd) after 1 hour. In 3 hours the flux was 1.05 $m^3/m^2/d$ (25.8 gfd), and after 3 days it was 0.82 $m^3/m^2/d$ (20.0 gfd) with a conductivity rejection of 27%. The low flux indicated a poor membrane, and the unit was shut down temporarily. The membrane was inadvertently left dry for about 2 weeks, and it was decided to try a Na_2CO_3 wash to see what improvement, if any, could be obtained. The unit was restarted (Run U-2) with fresh waste water (E_1) after the wash, achieving an initial flux of 1.78 $m^3/m^2/d$ (43.6 gfd) and a 42.9% conductivity rejection. After an hour of operation and a power failure related shutdown, the flux had dropped to 1.06 $m^3/m^2/d$ (25.9 gfd). As seen in Figure 35 and Table 10, the flux decreased gradually from its initial value and leveled off at about 0.75 $m^3/m^2/d$ (18.4 gfd). The rejections of color were good (94.3-99.1%), but the rejections of solids were much poorer than those obtained in Run U-1. There were a number of power failure related shutdowns during Run U-2, but these did not seem to have a significant impact upon the unit's performance. The problems with membrane performance seemed to be related more to problems with the formation step than with operational difficulties. On June 14, 1977, the unit was shut down to perform a wash sequence in an attempt to improve the membrane performance. A caustic wash (NaOH, pH = 11.8) and an acid wash (HNO_3, pH = 1.5) were performed, and an attempt to add a second membrane produced a flux of only 2.20 $m^3/m^2/d$ (54.1 gfd). Because this flux was still lower than desired, a second wash sequence with extended washing times was tried. As the flux did not improve, and new tube bundles were available, the unit was shut down, and the bundles removed.

Unfortunately, the newer tube bundles proved to have even larger outside diameters than the previous ones, and the bundles could not be loaded without breaking some of the tubes in the outer ring. Thirteen bundles were finally loaded, but most of these bundles had several outer tubes broken and stubbed off. It is certain that several bundles had tubes in contact with the piping, but it was impossible to load them any other way. This problem with oversized tubes was corrected later when the manufacturer replaced the worn extrusion die with which the tubes had been made. A membrane was formed and, when started up (Run U-3, Figure 36 and Table 10) with the waste water (E_1), it produced an initial flux of 3.98 $m^3/m^2/d$ (97.6 gfd). However, in only 14 hours the flux had dropped to 1.07 $m^3/m^2/d$ (26.2 gfd) and in 42 hours to 0.70 $m^3/m^2/d$ (17.1 gfd). This very rapid flux decline, plus the poor rejections of the solids in the concentrate stream, indicated another poor membrane, even though color rejections were good. The mill was shut down for a Fourth of July holiday and mill maintenance work, and the unit was idle until July 11, 1977. Fresh waste water (E_1) was then added to the system, and on startup a flux of 1.30 $m^3/m^2/d$ (32.0 gfd) was produced. The flux continued to drop for 2 days, at which time a wash sequence was performed. However, no improvement was obtained, and because a new module using porous carbon tubes (Union Carbide Corp.) became available, this run was abandoned and the ceramic tube bundles were removed. It was found that the old membranes could be removed from the ceramic tubes by heating to 105°C, but immersion in 1:1 HCl had no effect. It was observed that HCl-treated bundles did not lose their membrane when heated, indicating that the acid may have altered the membrane

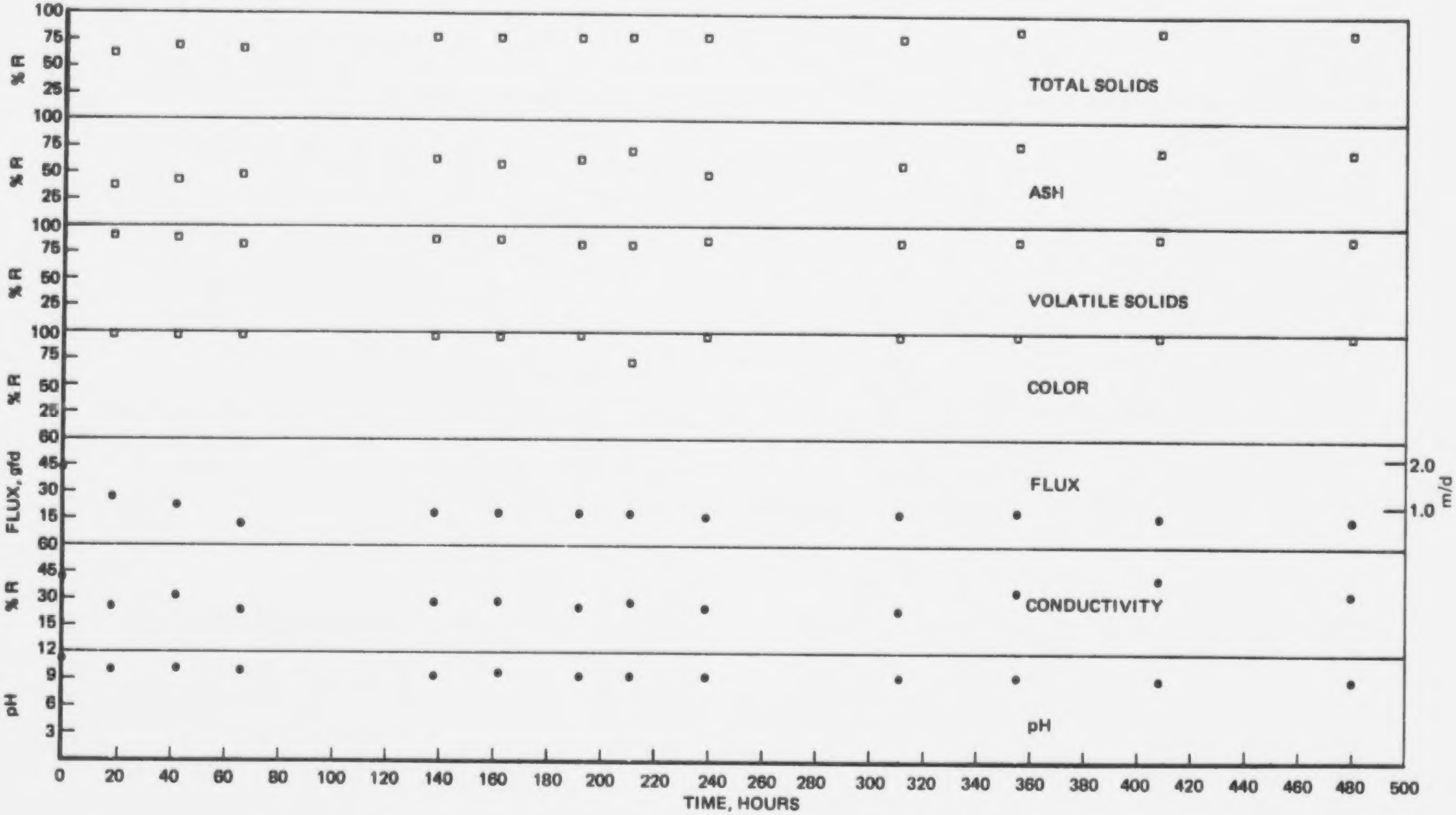


Figure 35. Run U-2. Ultrafiltration of caustic bleach effluent (E_1).

1.59×10^6 Pa 230 psig	4.57 m/s 15 ft/sec	52°C pH 9-11

(ACTUAL ELAPSED OPERATING TIME 361 HOURS.)

TABLE 10. ULTRAFILTRATION OF CAUSTIC BLEACH EFFLUENT, RUNS U-2 AND U-3

Date, 1977	Elapsed Operating Time, hr.	Flux, $m^3/m^2/d$ (gfd)	pH		Conductivity			Total Solids, p.p.m.		
			Concentrate	Permeate	Concentrate	Permeate	% R	Concentrate	Permeate	% R
			RUN U-2							
5/24	0.5	1.78 (43.6)	11.0	11.2	2800	1600	42.9	3052 (Raw Waste)		
5/25	18[1]	1.11 (27.2)	10.2	10.1	3800	2800	26.3	5163	1860	64.0
5/26	40	0.97 (23.8)	10.1	10.1	3700	2500	32.4	5976	1744	70.8
5/27	63[1]	0.50 (12.2)	9.9	9.8	5000	3800	24.0	8095	2652	67.2
5/30	132	0.75 (18.4)	9.6	9.5	5300	3800	28.3	13,550	2734	79.8
5/31	156	0.76 (18.7)	9.7	9.6	5400	3800	29.6	13,568	2864	78.9
6/1	180	0.77 (18.8)	9.4	9.3	5800	4300	25.9	15,421	3628	76.5
6/2	204	0.76 (18.7)	9.6	9.5	5900	4300	27.1	17,114	3620	78.5
6/3	233	0.67 (16.5)	9.4	9.3	6000	4500	25.0	18,585	4255	77.1
6/6	249[2]	0.74 (18.1)	9.1	9.1	6000	4550	24.2	18,542	4441	76.0
6/8	292	0.79 (19.3)	9.6	9.4	5150	3400	34.0	19,013	2931	85.6
6/10	336[1]	0.73 (17.8)	9.2	9.0	4500	2600	42.0	17,759	2332	86.9
6/13	361	0.64 (15.8)	9.2	9.0	5100	3400	33.3	20,249	2942	85.5
			RUN U-3							
6/28	0	3.98 (97.6)	Startup							
6/29	14	1.07 (26.2)	10.6	10.8	4900	3700	24.0	4801	2351	37.0
6/30	42	0.70 (17.1)	10.5	10.7	5550	4250	23.0	7579	3390	55.3

(continued)

Date, 1977	Elapsed Operating Time, hr.	Flux, $m^3/m^2/d$ (gfd)	Ash, p.p.m.			Volatile Solids, p.p.m.			Color, c.u.		
			Concentrate	Permeate	% R	Concentrate	Permeate	% R	Concentrate	Permeate	% R
			RUN U-2								
5/24	0.5	1.78 (43.6)	1821 (Raw Waste)			1231 (Raw Waste)			3860 (Raw Waste)		
5/25	18[1]	1.11 (27.2)	2671	1622	39.3	2492	238	90.4	14,800	171	98.8
5/26	40	0.97 (23.8)	2473	1364	44.8	3503	380	89.2	17,000	148	99.1
5/27	63[1]	0.50 (12.2)	3274	1768	46.0	4821	884	81.7	22,800	426	98.1
5/30	132	0.75 (18.4)	5147	1888	63.3	8403	848	89.9	57.400	592	99.0
5/31	156	0.76 (18.7)	4635	1941	58.1	8933	923	89.7	59,000	780	98.7
6/1	180	0.77 (18.8)	5659	2093	63.0	9762	1535	84.3	68,000	980	98.6
6/2	204	0.76 (18.7)	6186	1823	70.5	10,928	1797	83.6	79,000	4480	94.3
6/3	233	0.67 (16.5)	5674	2882	49.2	12,911	1373	89.4	82,800	1216	98.5
6/6	249[2]	0.74 (18.1	6199	2624	57.6	12,343	1812	85.3	92,600	1216	98.7
6/8	292	0.79 (19.3)	5960	1393	76.6	13,053	1538	88.2	98,400	990	99.0
6/10	336[1]	0.73 (17.8)	4634	1320	71.5	13,125	1012	92.3	100,000	900	99.1
6/13	361	0.64 (15.8)	5464	1500	72.5	14,785	1442	90.2	104,000	1190	98.9
			RUN U-3								
6/28	0	3.98 (97.6)	Startup								
6/29	14	1.07 (26.2)	1592	1489	6.5	3209	862	73.1	8000	463	94.2
6/30	42	0.70 (17.1)	2486	2007	19.3	5093	1383	72.8	16,300	690	95.8

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[1] Temporary shutdown due to power failure. Restarted.

[2] Shut down during weekend due to power failure. Restarted.

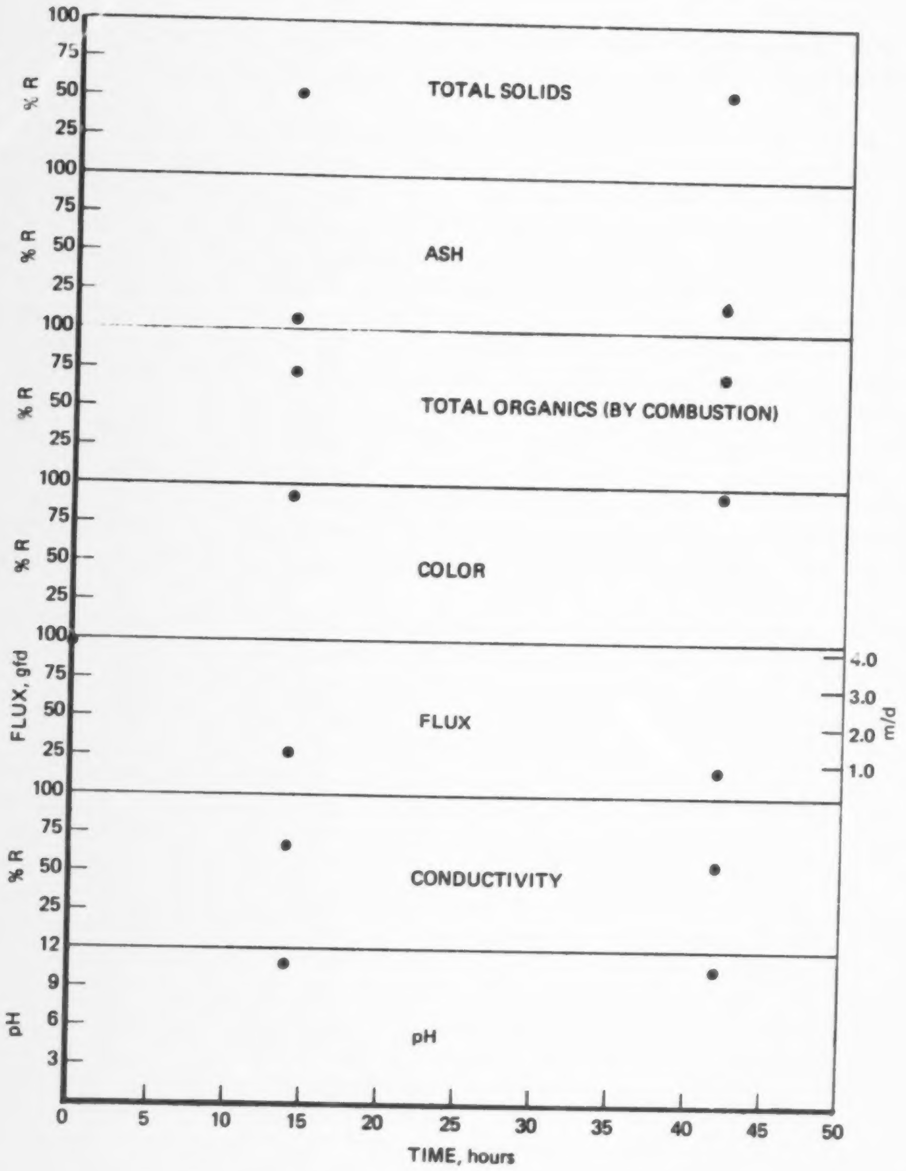

Figure 36. Run U-3. Ultrafiltration of caustic bleach effluent (E_1). Continuation of Run U-2 with new membrane and tubular supports.

1.59×10^6 Pa 230 psig	4.57 m/s 15 ft/sec	52°C

material in some way. Because these regenerated tubes were oversized, they were not reinstalled and the following Run U-4 was performed using only the carbon tube module.

The carbon tube module was built by Oak Ridge National Laboratory and consisted of a stainless steel shell containing Lucite^{TM}blocks with seven holes drilled through them. The holes were aligned to allow the carbon tubes to pass through and were of the proper diameter to allow free flow over the tube exterior. The tubes were suspended away from the Lucite^{TM} blocks with two spacer rings which were also cut to allow free flow past them. One end of each tube was sealed, and the other was cemented into a stainless steel threaded bushing which screwed into the end plate of the shell. This allowed passage of the permeate from the interior of the tube out of the shell. Each tube was 1.02 cm (0.4 in.) outside diameter and a nominal 127 cm. (50 in.) long, and with seven tubes installed in the module the total membrane surface area was 0.285 M^2 (3.07 sq. ft.). The module was mounted in place of the UCARSEP™ module and incorporated into the system during membrane formation and operation in the same manner as ceramic tubes. This unit's advantage was that it could be run at high pressures, up to 6.894×10^6 Pa (1000 psig) and higher, allowing its possible use as a reverse osmosis membrane support as well as an ultrafiltration support. The membrane formation and operation parameters were the same as those of the ceramic tube bundles, except that the concentrate flow rate was raised slightly to achieve the surface velocity of 4.57 m/s (15 ft/sec).

The first membrane was applied to the carbon tubes on July 22, 1977, and the unit started up using fresh waste water (E_1). The raw feed was filtered through a 5 μm rating filter bag and a slimicide, Metasol D3TA (Merck Chemical Co.), was added to prevent biological growths. The initial flux was 1.61 $m^3/m^2/d$ (39.6 gfd) with 19.7% conductivity rejection. Over the weekend, the flux dropped to 0.92 $m^3/m^2/d$ (22.5 gfd) and stayed at this level for 12 days. Unfortunately, there are no chemical data for this period because the samples were inadvertently discarded. The unit was shut down when the raw feed line from the bleach plant became clogged, and after a water rinse, the initial flux on startup with fresh E_1 was only 0.98 $m^3/m^2/d$ (24 gfd). The unit operated irregularly for several days because of controller problems and was shut down until late September. On September 26, 1977, a wash sequence was initiated in preparation for a new membrane formation. During the acid wash, total power was lost, and the entire unit was left filled with 0.5 $\underline{M}$ HNO_3 until October 10, 1977. When restarted with HNO_3 solution, the flux was initially 2.47 $m^3/m^2/d$ (60.7 gfd), rose to 3.46 $m^3/m^2/d$ (85 gfd) in about 1 hour, and after 2 more hours had dropped to 2.90 $m^3/m^2/d$ (71.2 gfd). The unit was drained, rinsed, and an additional layer of hydrous Si(IV) oxide applied. Upon restarting with fresh waste water on October 12, 1977, the initial flux was 1.41 $m^3/m^2/d$ (34.7 gfd). No Metasol was used in this or subsequent runs because it was theorized that the slimicide was adversely affecting the flux. The data from this run (U-4) are shown in Figure 37 and Table 11. The flux dropped gradually until October 17, 1977 when the leaking tank caused the level controller to add excess raw waste. The dilution and slightly lower solids concentration probably contributed to the flux increase. However, the flux and the total solids concentration rose even higher on October 18, 1977. The unit was found shut down on October 19, 1977 and restarted, but on October 20, 1977 the tank was found overflowing because of a jammed feed valve. The concentrate in the system was drained out and the unit refilled and restarted. The initial flux was 1.91 $m^3/m^2/d$ (46.8 gfd), but after 7 hours the flux had risen to 2.02 $m^3/m^2/d$ (49.6 gfd). The next day the flux held steady and rose slightly over the weekend.

The flux rates obtained were higher than those in Runs U-2 and U-3 but less than those of Run U-1. The soaking in HNO_3 and additional hydrous Si(IV) oxide seemed to improve the flux somewhat, although little change was noted in the rejection of the constituents. Overall color rejection

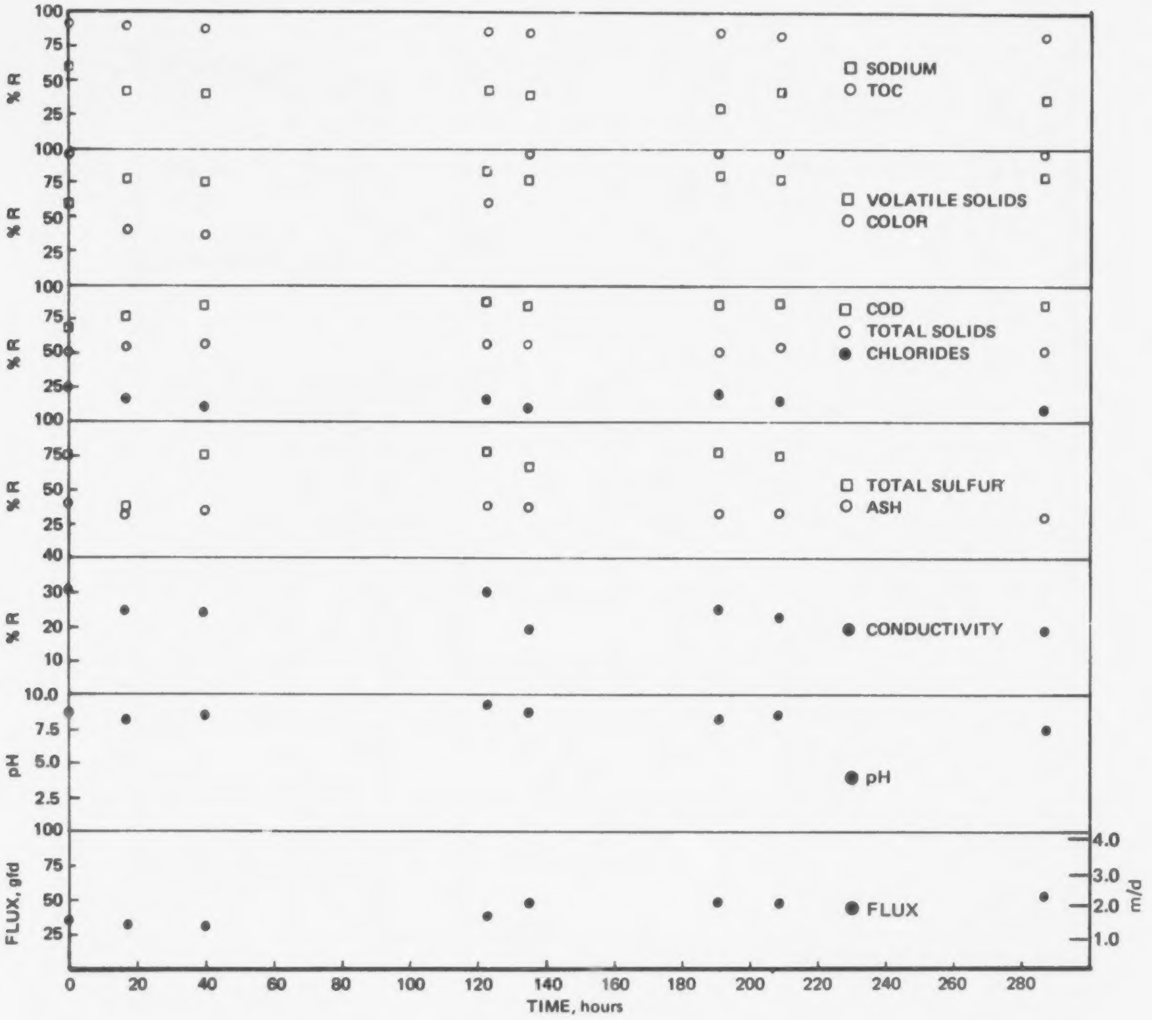

Figure 37. Run U-4. Ultrafiltration of caustic bleach effluent (E_1), carbon tube only.

1.52×10^6 Pa 220 psig	4.57 m/s 15 ft/sec	52°C pH 8-10

TABLE 11. ULTRAFILTRATION OF CAUSTIC BLEACH EFFLUENT USING CARBON TUBE MODULE, RUN U-4.

Date, 1977	Elapsed Operating Time, hr.	Flux, $m^3/m^2/d$ (gfd)	— pH — Concen-trate	Per-meate	Conductivity Concen-trate	Per-meate	% R	Total Solids, p.p.m. Concen-trate	Per-meate	% R	—Ash, p.p.m.— Concen-trate	Per-meate	% R	Chloride, p.p.m. Concen-trate	Per-meate	% R
10/12	8-1/3	1.45 (35.7)	8.75	8.85	4500	3100	31.1	4647	2187	52.9	1957	1147	41.4	1197	802	33.0
10/13	21[1]	1.33 (32.7)	8.50	8.40	4800	3600	25.0	5689	2504	56.0	2806	1820	35.1	1175	993	15.5
10/14	40	1.30 (32.0)	8.60	8.55	4900	3700	24.5	6804	2931	56.9	3502	2190	37.5	1259	1092	13.3
10/17	123[2]	1.56 (38.3)	9.25	9.15	4800	3350	30.2	6157	2548	58.6	3406	2144	37.1	1221	978	19.9
10/18	135[3]	1.89 (46.5)	8.85	8.70	5300	4250	19.8	8052	3456	57.1	3978	2540	36.2	1361	1193	12.3
10/20	191	2.02 (49.6)	8.35	8.45	4050	3000	25.9	4482	2129	52.5	2552	1744	31.2	1039	844	23.1
10/21	209	1.99 (48.9)	8.60	8.50	4350	3350	23.0	5690	2508	55.9	2939	1918	34.7	1072	896	16.4
10/24	287	2.21 (54.3)	7.90	7.50	3800	3050	19.7	4787	2207	53.9	2574	1784	30.7	896	806	10.0

(continued)

Date, 1977	Elapsed Operating Time, hr.	Flux, $m^3/m^2/d$ (gfd)	— Color, c.u. — Concen-trate	Per-meate	% R	Sodium, p.p.m., as Na Concen-trate	Per-meate	% R	— 5-Day BOD, p.p.m. — Concen-trate	Per-meate	% R	— COD, p.p.m. — Conden-trate	Per-meate	% R
10/12	8-1/3	1.45 (35.7)	7450	113	98.5	1001.2	383.2	61.7	370	88	76.2	1522	440	71.1
10/13	21[1]	1.33 (32.7)	10,440	5940	41.1	1295.3	763.2	41.1	–	–	–	2499	581	76.8
10/14	40	1.30 (32.0)	12,450	7550	39.4	1409.6	854.1	39.4	–	–	–	4060	510	87.4
10/17	123[2]	1.56 (38.3)	13,850	5050	63.5	1375.6	778.0	43.4	–	–	–	3407	387	88.6
10/18	135[3]	1.89 (46.5)	10,200	150	98.5	1726.5	994.6	42.4	–	–	–	5130	653	87.3
10/20	191	2.02 (49.6)	9500	179	98.1	982.7	677.9	31.0	–	–	–	2251	286	87.3
10/21	209	1.99 (48.9)	10,200	150	98.5	1168.4	664.6	43.1	–	–	–	3291	407	87.6
10/24	287	2.21 (54.3)	9500	179	98.1	977.0	600.0	38.6	–	–	–	2710	369	86.4

(continued)

Date, 1977	Elapsed Operating Time, hr.	Flux, $m^3/m^2/d$ (gfd)	— TOC, p.p.m. — Concen-trate	Per-meate	% R	— Total Sulfur, p.p.m. — Concen-trate	Per-meate	% R	Volatile Solids, p.p.m. Concen-trate	Per-meate	% R
10/12	8-1/3	1.45 (35.7)	775	57	92.6	12	3.0	75.0	2690	1040	61.3
10/13	21[1]	1.33 (32.7)	1080	94	91.3	16	6.0	37.5	2883	684	76.3
10/14	40	1.30 (32.0)	1463	150	89.7	26	6.0	76.9	3302	741	77.6
10/17	123[2]	1.56 (38.3)	1170	150	87.2	17	3.5	79.4	2751	404	85.3
10/18	135[3]	1.89 (46.5)	1890	277.4	85.3	22	7.0	68.2	4074	916	77.5
10/20	191	2.02 (49.6)	904	128.2	85.8	14	3.0	78.6	1930	385	80.1
10/21	209	1.99 (48.9)	1186	184.0	84.5	17	4.0	76.5	2751	590	78.6
10/24	287	2.21 (54.3)	1088	170.2	84.4	–	–	–	2213	423	80.9

[1] Concentrate tank leaking. Some loss of concentrate feed.

[2] Unit shut down on 10/19/77 due to clogged feed line. Restarted.

[3] Level control failure. Drained tank and restarted with fresh feed.

in Run U-4 was good, but it was not as high as with the ceramic tubes and the "good" membrane used in Run U-1. The fair to good rejections of volatile solids, TOC, total sulfur, and COD, and the low rejections of sodium ash and chlorides indicate that this ultrafiltration process for treating bleach plant wastes is a valid concept, even when operation is not optimal. The large organic molecules are being retained, while the chlorides are being passed.

The unit was found shutdown on October 25, 1977 because of a power failure. As ceramic tube bundles were now available, they were installed after a water rinse. The unit was filled with a NaOH solution (pH = 12.9) and allowed to run overnight. On stopping the wash and rinsing the unit out with mill supply water, it was observed that the flux from the ceramic tubes had dropped dramatically, almost as if a membrane had been formed. Apparently the materials that washed out of the piping were deposited on the porous tubes, in a similar manner to that of studies on lignin membranes. An acid wash lasting over 3 hours had little effect because the flux during the deionized water rinse that followed was only 4.36 $m^3/m^2/d$ (107 gfd), as compared with the high fluxes (81.48 $m^3/m^2/d$ [2000 gfd]) expected for new tube bundles. Because no other tube bundles were then available, a membrane was applied on the ceramic tubes. The carbon tube bundle was isolated during the membrane formation step. The flux for the ceramic tubes was 4.25 $m^3/m^2/d$ (104.3 gfd) at the end of the hydrous Si(IV) oxide layer formation. The unit was filled with fresh waste water (E_1) and started up, using both the carbon tubes and ceramic tube bundles. The data for the ceramic tubes is given as Run U-5 and for the carbon tubes as Run U-6; however, the runs occurred simultaneously and were treating the same feed.

The data for Run U-5 are given in Figure 38 and Table 12. The initial flux on startup was 2.75 $m^3/m^2/d$ (67.4 gfd), but it dropped slightly within 30 minutes to 2.59 $m^3/m^2/d$ (63.6 gfd) and leveled out the next several days at slightly below 2.04 $m^3/m^2/d$ (50 gfd). The unit was shutdown on November 4, 1977 because of poor permeate quality. The fluxes from the individual bundles ranged from 1.36 to 2.72 $m^3/m^2/d$ (33.4 to 66.7 gfd). The color removal from different bundles varied widely also, but no correlation was evident between flux and color removal. The bundles with the lowest fluxes did not give higher color rejections than those with the highest fluxes. The unit was washed using the regular procedure and left for the weekend with the 0.5 $\underline{N}$ HNO_3 (pH = 1.1) solution in it. A layer of hydrous Si(IV) oxide was applied to both the ceramic and carbon tubes, and the unit restarted with fresh waste water (E_1). The initial flux was 2.66 $m^3/m^2/d$ (65.4 gfd), but the flux rose in 2 hours to 3.02 $m^3/m^2/d$ (74.2 gfd). The unit ran on an irregular schedule for several days because of power failures, tank leaks, and loss of feed. On November 16, 1977, the unit was producing very dark permeates, and the unit was shut down until November 28, 1977 for cleanup and new membrane.

The additional membrane produced an initial flux of 2.77 $m^3/m^2/d$ (68.1 gfd), but within 1 day the flux rose to 3.47 $m^3/m^2/d$ (85.1 gfd). The permeates were dark brown in appearance, but the data in Table 12 show that the unit was achieving good rejections of color and organics while progressively concentrating the total solids. This dark color in the permeate and the shortage of time forced the shutdown of the unit on December 7, 1977. The data shown in Table 12 indicate that this last membrane was a fairly good one because high fluxes 4.07 $m^3/m^2/d$ (100 gfd) were possible with good rejections. While the overall performance of the membrane was not quite as good as Run U-1, the unit's performance could be improved under less than ideal conditions. This ability to adjust to problems encountered and to regenerate the membranes is perhaps the greatest advantage to using dynamically formed membranes. The last membrane addition resulted in improved rejections and higher fluxes.

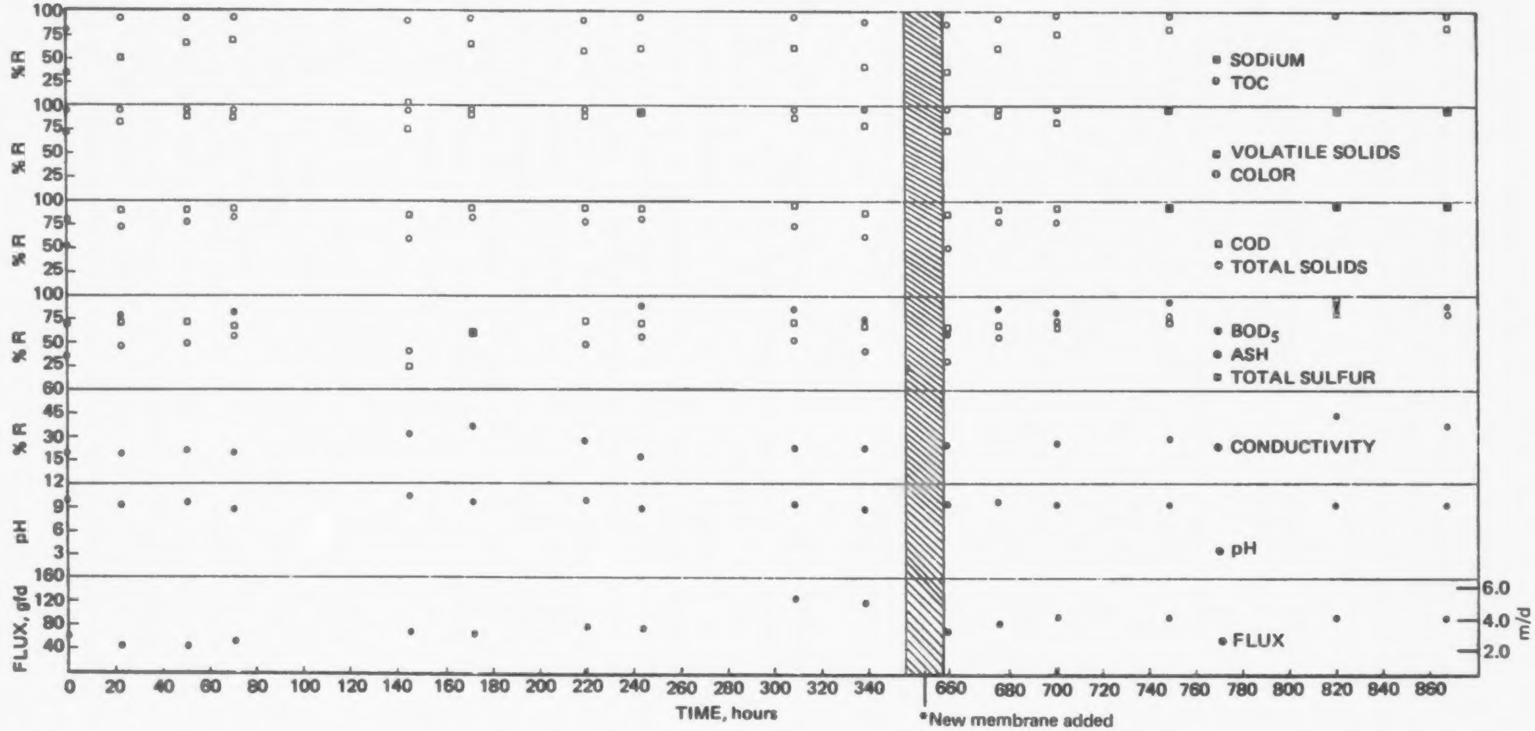

Figure 38. Run U-5. Ultrafiltration of caustic bleach effluent (E_1) using ceramic bundles.

1.59×10^6 Pa	4.57 m/s	$52^{o}C$
230 psig	15 ft/sec	pH 8-10

TABLE 12. ULTRAFILTRATION OF CAUSTIC BLEACH EFFLUENT USING CERAMIC MEMBRANE SUPPORT, RUN U-5

Date, 1977	Elapsed Operating Time, hr.	Flux, m³/m²/d (gfd)	pH		Conductivity			Total Solids, p.p.m.			Ash, p.p.m.			Chloride, p.p.m.		
			Concen-trate	Per-meate	Concen-trate	Per meate	% R	Concen-trate	Per-meate	% R	Concen-trate	Per-meate	% R	Concen-trate	Per-meate	% R
11/1	1	2.59 (63.6)	10.10	10.10	4800	3800	20.8	5084	2388	53.0	2910	1808	37.9	975	822	15.7
11/2	23	1.93 (47.3)	9.50	0.50	5250	4250	19.0	12,150	3597	70.4	4311	2363	45.2	–	–	–
11/3	51[1]	1.89 (46.4)	9.60	9.60	5850	4600	21.4	21,434	4413	79.4	5745	2726	52.6	–	–	–
11/4	71	2.01 (49.4)	8.85	8.80	5200	4150	20.2	21,736	3910	82.0	5211	2161	58.5	–	–	–
11/7	145	2.92 (71.8)	10.50	10.60	3500	2400	31.4	3349	1332	60.2	1668	931	44.2	941	571	39.3
11/8	170[2]	2.66 (65.4)	9.65	9.60	4100	2600	36.6	10,127	1809	82.1	2933	1149	60.8	–	–	–
11/10	220	3.12 (76.7)	9.75	9.80	6100	4400	27.9	20,739	4229	79.6	5525	2848	48.5	–	–	–
11/11	244[3]	3.02 (74.2)	8.80	8.80	6700	5500	17.9	32,576	5630	82.7	8404	3662	56.4	–	–	–
11/14	309	5.04 (123.6)	9.35	9.20	4850	3750	22.7	14,869	2995	79.9	4043	1875	53.6	753	745	1.1
11/15	339[4]	4.80 (117.9)	8.80	8.60	3500	2700	22.9	5944	2104	64.6	2328	1374	41.0	772	658	14.8
11/28	652	2.77 (68.1)	9.60	9.45	4650	3500	24.7	5484	2694	50.9	2946	2006	31.9	1050	934	11.0
11/29	676[5]	3.47 (85.1)	9.55	9.60	4100	4100	–	17,711	3653	79.4	5557	2452	55.9	–	–	–
11/30	701	3.74 (91.7)	9.65	9.40	4350	3250	25.3	21,498	4701	78.1	5588	1598	71.4	–	–	–
12/2	749	3.74 (91.7)	9.10	9.10	5100	3600	29.4	36,636	3169	91.4	7717	1859	75.9	–	–	–
12/5	820	4.04 (99.3)	8.90	9.10	4500	2500	44.4	41,277	2375	94.3	7922	1316	83.5	–	–	–
12/7	867	4.04 (99.3)	9.85	10.10	5200	3200	38.5	52,036	3039	94.2	10,791	1744	83.8	–	–	–

(continued)

Date, 1977	Elapsed Operating Time, hr.	Flux, m³/m²/d (gfd)	Color, c.u.			Sodium, p.p.m., as Na			5-Day BOD, p.p.m.			COD, p.p.m.		
			Concen-trate	Per-meate	% R	Concen-trate	Per meate	% R	Concen-trate	Per-meate	% R	Concen-trate	Per-meate	% R
11/1	1	2.59 (63.6)	7450	243	96.7	1051.6	666	36.7	–	–	–	2614	465	82.2
11/2	23	1.93 (47.3)	41,750	890	97.9	1826	860	52.9	1320	300	77.3	9934	980	90.1
11/3	51[1]	1.89 (46.4)	84,000	1800	97.9	2429	773	68.2	–	–	–	19,600	1360	93.1
11/4	71	2.01 (49.9)	48,000	1800	96.3	1924	538	72.0	2100	350	83.3	29,375	1400	94.2
11/7	145	2.92 (71.8)	2600	68	97.4	418	402	3.8	–	–	–	1700	220	87.1
11/8	170[2]	2.66 (65.4)	39,100	510	98.7	1530	508	66.8	–	–	–	8400	490	94.2
11/10	220	3.12 (76.7)	89,000	2040	97.7	2944	1157	60.7	–	–	–	22,500	1310	94.2
11/11	244[3]	3.02 (74.2)	159,000	4100	97.4	3973	1505	62.1	4400	590	86.6	39,000	2050	94.7
11/14	309	5.04 (123.6)	61,000	1420	97.7	2136	802	62.5	1700	240	85.9	15,600	730	95.3
11/15	339[4]	4.80 (117.9)	14,600	482	96.7	968	537	44.0	810	220	72.8	4425	540	87.8
11/28	652	2.77 (68.1)	10,900	273	97.5	1129	729	35.4	560	220	60.7	3100	460	85.2
11/29	676[5]	3.47 (85.1)	83,000	1610	98.1	2411	881	63.5	2600	340	86.9	15,500	1135	92.7
11/30	701	3.74 (91.7)	110,500	1730	98.4	2833	652	77.0	1800	300	83.3	26,875	1380	94.9
12/2	749	3.74 (91.7)	207,000	2840	98.6	4019	834	79.3	5000	360	92.8	49,400	1375	97.2
12/5	820	4.04 (99.3)	232,000	2750	98.8	–	–	–	4700	380	91.9	52,800	1330	97.5
12/7	867	4.04 (99.3)	291,000	4500	98.5	4749	731	84.6	3600	360	90.0	66,800	1550	97.7

[1] Unit shut down because of poor permeate quality. Additional Si(IV) oxide membrane added, restarted.

[2] Unit down all day (11/9/77) due to power failure. Restarted 11/10/77.

[3] Tank leak forced shutdown. Restarted 11/15/77.

[4] Unit shut down to apply new membrane. Startup delayed until 11/28/77 due to tank and other repairs.

[5] Tank found overflowing. Raw feed valve jammed open and dilution of concentrate occurred, restarted.

(continued)

TABLE 12 (continued)

Date, 1977	Elapsed Operating Time, hr.	Flux, $m^3/m^2/d$ (gfd)	TOC, p.p.m. Concen-trate	TOC, p.p.m. Per-meate	TOC, p.p.m. % R	Total Sulfur, p.p.m. Concen-trate	Total Sulfur, p.p.m. Per-meate	Total Sulfur, p.p.m. % R	Volatile Solids, p.p.m. Concen-trate	Volatile Solids, p.p.m. Per-meate	Volatile Solids, p.p.m. % R
11/1	1	2.59 (63.6)	995	181.2	81.8	17	5.0	70.6	2174	580	73.3
11/2	23	1.93 (47.3)	3505	306	91.3	46	13.0	71.7	7839	1234	84.3
11/3	52[1]	1.89 (46.4)	8420	555	93.4	76	20.0	73.7	15,689	1687	89.3
11/4	71	2.01 (49.4)	8750	540	93.8	33.1	11.0	66.8	16,525	1330	89.8
11/7	145	2.92 (71.8)	690	66	90.4	8.9	6.6	25.8	1681	401	76.2
11/8	170[2]	2.66 (65.4)	3575	188	94.7	27.3	8.5	68.9	7194	660	90.8
11/10	220	3.12 (76.7)	5550	555	90.0	42.5	11.2	73.6	15,214	1381	90.9
11/11	244[3]	3.02 (74.2)	13,663	953	93.0	56.9	16.0	71.9	24,172	1968	91.9
11/14	309	5.04 (123.6)	5472	425	92.1	27.3	7.9	71.1	10,826	1120	89.7
11/15	339	4.80 (117.9)	1650	220	86.7	13.2	4.1	68.9	3616	730	79.8
11/28	652	2.77 (68.1)	1160	165	85.8	23.1	8.6	62.8	2538	638	74.9
11/29	676[4]	3.47 (85.1)	6921	513	92.6	44.0	14.3	67.5	12,154	1201	90.1
11/30	701	3.74 (91.7)	10,160	502	95.1	40.1	12.4	69.1	15,910	3103	80.5
12/2	749	3.74 (91.7)	16,814	595	96.5	45.7	12.9	71.8	28,919	1310	95.5
12/5	820	4.04 (99.3)	19,137	505	97.4	14.0	1.0	92.9	33,355	1059	96.8
12/7	867	4.04 (99.3)	24,075	765	96.8	—	—	—	41,240	1295	96.9

[1] Unit shut down because of poor permeate quality. Additional Si(IV) oxide membrane added, restarted.

[2] Unit down all day (11/9/77) due to power failure. Restarted 11/10/77.

[3] Tank leak forced shutdown. Restarted 11/15/77.

[4] Unit shut down to apply new membrane. Startup delayed until 11/28/77 due to tank and other repairs.

[5] Tank found overflowing. Raw feed valve jammed open and dilution of concentrate occurred, restarted.

The series of events is identical for Run U-6 (the carbon tube module) as for Run U-5. The initial flux on startup was 1.87 m^3/m^2/d (46.0 gfd), but this dropped to 1.54 m^3/m^2/d (37.9 gfd) in 30 minutes. The flux rose slightly and remained stable for several days. The permeate color became dark, and the unit was shut down in preparation for an additional membrane layer. The unit was left full of 0.5 N HNO_3 (pH = 1.1) over the weekend, and a layer of hydrous Si(IV) oxide was applied. The initial flux upon restarting with fresh waste water (E_1) was 1.45 m^3/m^2/d (35.7 gfd), with an increase to 1.84 m^3/m^2/d (45.3 gfd) in 2 hours. The unit ran on an irregular schedule for several days because of tank repairs and power failure, but the flux gradually increased. On November 16, 1977, the permeate quality appeared to be poor, so the unit was shut down for cleanup and a new membrane formation. The startup with the new membrane was delayed until November 28, 1977 by necessary repairs.

The initial flux on startup was 1.80 m^3/m^2/d (44.3 gfd), and the flux gradually rose over the rest of the run. The rejections of organics and solids improved slightly with the addition of the last membrane, as seen in Figure 39 and Table 13. The carbon and ceramic tube supports did not appear to have any distinct advantage over one another with regard to rejections, but the ceramic supports gave slightly higher fluxes. As with the ceramic tubes, flux and rejection performance was increased by adjustments to the dynamic membranes.

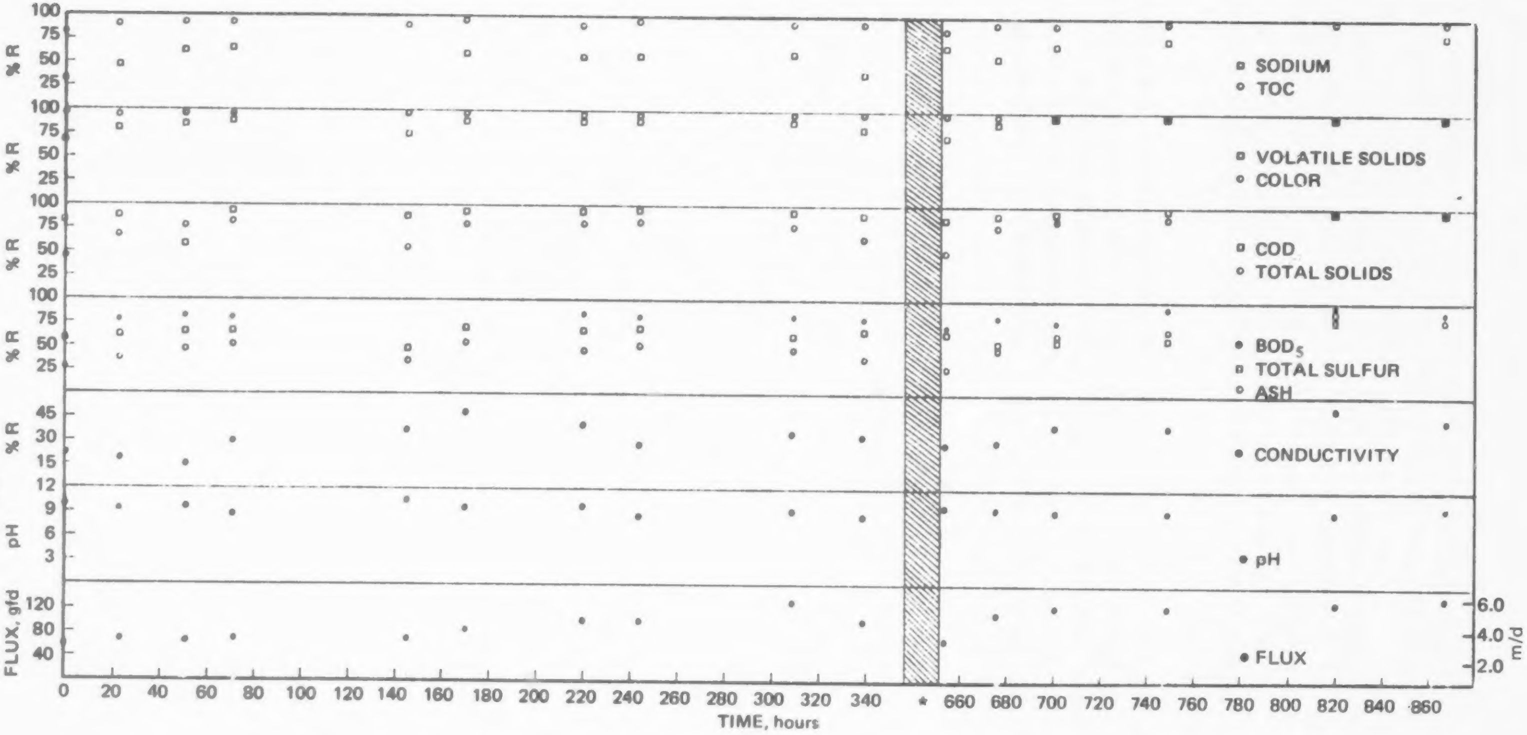

Figure 39. Run U-6. Ultrafiltration of caustic bleach effluent (E_1) using carbon tube module.

1.59 x 10^6 Pa
230 psi

4.57 m/s
15 ft/sec

52°C
pH 8-10

*New membrane applied.

TABLE 13. ULTRAFILTRATION OF CAUSTIC BLEACH EFFLUENT USING CARBON MEMBRANE SUPPORT, RUN U-6.

Date, 1977	Elapsed Operating Time, hr.	Flux, $m^3/m^2/d$ (gfd)	pH		Conductivity			Total Solids, p.p.m.			Ash, p.p.m.			Chloride, p.p.m.		
			Concen-trate	Per-meate	Concen-trate	Per-meate	% R	Concen-trate	Per-meate	% R	Concen-trate	Per-meate	% R	Concen-trate	Per-meate	% R
11/1	1	1.54 (37.9)	10.10	10.10	4800	4050	15.6	5084	2765	45.6	2910	2099	27.9	975	932	4.4
11/2	23	1.68 (41.3)	9.50	9.50	5250	4550	13.3	12,150	4053	66.6	4311	2596	39.8	–	–	–
11/3	51[1]	1.64 (40.4)	9.60	9.65	5850	5250	10.3	21,434	5096	76.2	5745	3035	47.2	–	–	–
11/4	71	1.73 (42.5)	8.85	8.80	5200	4150	20.2	21,736	3910	82.0	5211	2381	54.3	–	–	–
11/7	145	1.83 (44.8)	10.50	10.60	3500	2600	25.7	3349	1477	55.9	1668	1072	35.7	941	549	41.7
11/8	170[2]	2.16 (53.1)	9.65	9.65	4100	2750	32.9	10,127	1981	80.4	2933	1296	55.8	–	–	–
11/10	220	2.53 (62.0)	9.75	9.85	6100	4400	27.9	20,739	4159	80.0	5525	2871	48.0	–	–	–
11/11	244[3]	2.53 (62.0)	8.80	8.80	6700	5400	19.4	32,576	5817	82.1	8404	3857	54.1	–	–	–
11/14	309	3.44 (84.5)	9.35	9.30	4850	3700	23.7	14,869	3189	78.6	4043	2068	48.9	–	–	–
11/15	339[4]	2,53 (62.0)	8.80	8.70	3500	2700	22.9	5944	2082	65.0	2328	1418	39.1	772	720	6.7
11/28	562	1.80 (44.3)	9.60	9.70	4650	3750	19.4	5484	2724	50.3	2946	2085	29.2	1050	975	7.1
11/29	676[5]	2.91 (71.5)	9.55	9.65	5500	4350	20.9	17,711	4162	76.5	5557	2780	50.0	–	–	–
11/30	701	3.15 (77.4)	9.40	9.40	4800	3500	27.1	21,498	3080	85.7	5588	1972	64.7	–	–	–
12/2	749	3.15 (77.4)	9.10	9.15	5100	3700	27.5	36,636	3691	89.9	7717	2287	70.4	–	–	–
12/5	820	3.44 (84.5)	8.90	9.05	4500	2900	35.6	41,277	2656	93.6	7922	1543	80.5	–	–	–
12/7	867	3.61 (88.5)	9.85	10.05	5200	3600	30.8	52,036	3754	92.8	10,791	2378	78.0	–	–	–

(continued)

Date, 1977	Elapsed Operating Time, hr.	Flux, $m^3/m^2/d$ (gfd)	Color, c.u.			Sodium, p.p.m., as Na			5-Day BOD, p.p.m.			COD, p.p.m.		
			Concen-trate	Per-meate	% R	Concen-trate	Per-meate	% R	Concen-trate	Per-meate	% R	Concen-trate	Per-meate	% R
11/1	1	1.54 (37.9)	7450	154	97.9	1051	716	31.9	–	–	–	2614	445	83.0
11/2	23	1.68 (41.3)	41,750	900	97.8	1826	976	46.6	1320	270	79.5	9934	1060	89.3
11/3	51[1]	1.64 (40.4)	84,000	2060	97.6	2429	879	63.8	2000	390	80.5	19,600	8075	58.8
11/4	71	1.73 (42.5)	48,000	1800	96.3	1924	665	65.4	2100	420	80.0	29,375	1575	94.6
11/7	145	1.83 (44.8)	2600	53	98.0	–	–	–	–	–	–	1700	180	89.4
11/8	170[2]	2.16 (53.1)	39,100	301	99.2	1530	571	62.7	–	–	–	8400	440	94.8
11/10	220	2.53 (62.0)	89,500	1164	98.7	2944	1268	56.9	2100	310	85.2	22,500	1185	94.7
11/11	244[3]	2.53 (62.0)	159,000	2540	98.4	3973	1649	58.5	4400	670	84.8	39,000	1860	95.2
11/14	309	3.44 (84.5)	61,000	820	98.7	2136	853	60.1	1700	310	81.8	15,600	895	94.3
11/15	339[4]	2.53 (62.0)	14,600	103	99.3	958	579	39.6	810	160	80.3	4425	370	91.6
11/28	652	1.80 (44.3)	10,900	102	99.1	1129	365	67.7	560	145	74.1	3100	365	88.2
11/29	676[5]	2.91 (71.5)	83.000	1540	98.1	2411	1035	57.1	2600	420	83.9	15,500	1265	91.8
11/30	701	3.15 (77.4)	110,500	1540	98.6	2833	794	72.0	1800	380	78.9	26,875	1380	94.9
12/2	749	3.15 (77.4)	207,000	2840	98.6	4019	891	77.8	5000	400	92.0	49,400	1380	97.2
12/5	820	3.44 (84.5)	232,000	2410	99.0	–	–	–	4700	350	92.6	52,800	1460	972
12/7	867	3.61 (88.5)	291,000	2750	99.1	4749	853	82.0	3600	390	89.2	66,800	1650	97.5

[1] Unit shut down because of poor permeate quality. Additional Si(IV) oxide membrane added, restarted.

[2] Unit down all day (11/9/77) due to power failure. Restarted 11/10/77.

[3] Tank leak forced shutdown. Restarted 11/15/77.

[4] Unit shut down to apply new membrane. Startup delayed until 11/28/77 due to tank and other repairs.

[5] Tank found overflowing. Raw feed valve jammed open and dilution of concentrate occurred, restarted.

(continued)

TABLE 13 (continued)

Date, 1977	Elapsed Operating Time, hr.	Flux, $m^3/m^2/d$ (gfd)	TOC, p.p.m. Concentrate	TOC, p.p.m. Permeate	TOC, p.p.m. % R	Total Sulfur, p.p.m. Concentrate	Total Sulfur, p.p.m. Permeate	Total Sulfur, p.p.m. % R	Volatile Solids, p.p.m. Concentrate	Volatile Solids, p.p.m. Permeate	Volatile Solids, p.p.m. % R
11/1	1	1.54 (37.9)	995	171.6	82.8	17	5	58.8	2174	666	69.4
11/2	23	1.68 (41.3)	3505	317.4	90.9	46	18	60.9	7839	1457	81.4
11/3	51[1]	1.64 (40.4)	8420	684.0	91.9	76	26	65.8	15,689	2161	86.2
11/4	71	1.73 (42.5)	8750	640.0	92.7	33.1	10.9	67.1	16,525	1529	90.8
11/7	145	1.83 (44.8)	690	66.0	90.4	8.9	4.6	48.3	1681	405	75.9
11/8	170[2]	2.16 (53.1)	3575	148.0	95.9	27.3	7.8	71.4	7194	670	90.7
11/10	220	2.53 (62.0)	5550	556.0	90.0	42.5	13.7	67.8	15,214	1288	91.5
11/11	244[3]	2.53 (62.0)	13,663	609.0	95.5	56.9	17.0	70.1	24,172	1960	91.9
11/14	309	3.44 (84.5)	5472	371.0	93.2	27.3	9.7	69.5	10,826	1121	89.7
11/15	339[4]	2.53 (62.0)	1650	135.0	91.8	13.2	4.0	69.7	3616	664	81.6
11/28	652	1.80 (44.3)	1160	158.0	86.4	23.1	8.0	65.4	2538	639	74.8
11/29	676[5]	2.91 (71.5)	6921	585.0	91.5	44.0	19.0	56.8	12,154	1382	88.6
11/30	701	3.15 (77.4)	10,160	578.0	94.3	40.1	16.0	61.1	15,910	1108	93.0
12/2	749	3.14 (77.4)	6814	705.0	95.8	45.7	18.1	60.4	28,919	1404	95.2
12/5	820	3.44 (84.5)	19,137	559	97.1	14.0	1.0	92.9	33,355	1113	96.7
12/7	867	3.61 (88.5)	24,075	700	97.1	–	–	–	41,240	1356	96.7

[1] Unit shut down because of poor permeate quality. Additional Si(IV) oxide membrane added, restarted.

[2] Unit down all day (11/9/77) due to power failure. Restarted 11/10/77.

[3] Tank leak forced shutdown. Restarted 11/15/77.

[4] Unit shut down to apply new membrane. Startup delayed until 11/28/77 due to tank and other repairs.

[5] Tank found overflowing. Raw feed valve jammed open and dilution of concentrate occurred, restarted.

SECTION 7

DISCUSSION OF RESULTS

REVERSE OSMOSIS UNIT

The pilot plant unit did not prove reliable enough to provide long-term operation data, but the trials did produce useful information in spite of the mechanical difficulties. The major parameters of interest are the fluxes obtained and the rejections of various constituents achieved by this type of membrane system. Most commercially available reverse osmosis units are capable of removing organic and inorganic solutes, but at low flux rates, usually 0.407 to 0.611 $m^3/m^2/d$ (10-15 gfd). Most types have limitations on temperature and pH as well. The dynamic membrane system is potentially useful for waste-water treatment because higher fluxes and at least equivalent removals are possible.

Run H-1 started with an initial flux of 2.35 $m^3/m^2/d$ (57.6 gfd), and the flux declined to 1.31 $m^3/m^2/d$ (32.2 gfd) after 95 hours of operation and 0.81 $m^3/m^2/d$ (19.8 gfd) after 238 hours. This run did not last long enough to determine the upper limit on solids concentration in the concentrated feed, but excellent rejections of solids and color were obtained (see Table 14). Run H-2 was begun after the membrane had been left dry for 2 weeks, and the fluxes and rejections were not as high overall as in Run H-1. The initial flux was higher than Run H-1 (3.30 $m^3/m^2/d$ [81.0 gfd]) but dropped to 1.53 $m^3/m^2/d$ (37.6 gfd) after only 18 hours. At 97 hours of operation the flux was only 0.46 $m^3/m^2/d$ (11.3 gfd) compared with the value (1.31 $m^3/m^2/d$ [32.2 gfd]) for Run H-1. The flux for this membrane dropped more rapidly and leveled off at a lower value than Run H-1, indicating that the drying out of the polyacrylic acid layer had adversely affected performance. As seen in Table 14, the rejections of the various constituents were lower also. Run H-3 was started with a membrane that was apparently affected by soluble iron in the membrane formation step. The initial flux was 4.12 $m^3/m^2/d$ (101.1 gfd) with contaminated permeate and 3.72 $m^3/m^2/d$ 91.3 gfd) after the permeate had cleared. This membrane was lost because of breakage and was replaced with a second membrane that gave an initial flux of 3.95 $m^3/m^2/d$ (67.0 gfd) within 17 hours that dropped to 1.40 $m^3/m^2/d$ (34.4 gfd) in 67 hours. The rejections during this run varied somewhat but were generally high, as seen in Table 14.

The effect of a wash sequence upon membrane performance was seen in two instances. In Run H-2, a Na_2CO_3 (pH = 10.6) solution that was used to wash the membrane raised the flux from 1.31 $m^3/m^2/d$ (32.2 gfd) to 1.80 $m^3/m^2/d$ (44.2 gfd). Unfortunately, the tube bundles were broken before further operation could be started. Another attempt at washing the membrane was made during Run H-3, using a NaOH (pH = 11.9) solution. The flux was raised to 1.74 $m^3/m^2/d$ (42.8 gfd), but it dropped to 1.09 $m^3/m^2/d$ (26.7 gfd) within 1 day of operation. Unfortunately, the unit was shut down before the effect of the wash on the rejections could be observed.

TABLE 14. SUMMARY OF REVERSE OSMOSIS DATA

	Run H-1	Run H-2	Run H-3
% Rejection of			
Conductivity	81.0 - 95.3	76.9 - 88.2	51.5 - 98.3
Total solids	97.8 - 99.6	91.2 - 95.0	88.7 - 97.2
Ash	96.5 - 99.1	89.9 - 96.5	86.6 - 98.9
Volatile solids	99.4 - 100.0	94.3 - 92.3	87.4 - 97.1
Color	99.9 - 100.0	97.8 - 99.8	98.2 - 100.0
Chlorides	79.2 - 92.9	N/A	84.5 - 91.7
Sodium	N/A	N/A	82.9 - 99.7
BOD_5	N/A	N/A	72.4 - 90.6
COD	N/A	N/A	60.3 - 95.2
TOC	N/A	N/A	25.4 - 95.1
Total sulfur	N/A	N/A	90.1 - 98.6

Note: N/A = Not available.

It is evident from the problems encountered during this study that the membrane formation step has not been optimized. In each run, more membrane forming material was used during the laboratory trials than should have been necessary. The reason for this is unknown, but it is possibly attributable to false fluxes during the formation step because of the weak spots in the membrane at points where the tubes rub each other and/or the piping. The higher apparent flux caused by these spots could falsely indicate that more membrane material is needed, while the bulk of the tube surface is coated too heavily. This could adversely affect the flux rate. Another interesting phenomenon observed during this study was that the permeate flow is initially dark and contaminated on startup of the unit; this occurred just after new membrane formation as well as after an intermittent shutdown. The permeate quality gradually improved until a very clear solution was obtained, usually after approximately 20 minutes. The flux at startup is also slightly higher before the permeate clears. The reason for this phenomenon is unknown but is possibly caused by compaction of the polyacrylic acid layer or by the formation of a wood-chemical type membrane. This could also be connected with the sudden drop in flux in Run H-2, which resulted in the membrane being dried out. The constituents in the waste water could have filled in membrane defects, causing a drop in flux. It must be emphasized that these theories have not been confirmed because of the operational problems encountered.

During the course of these trials, several points relative to the design of dynamic membrane reverse osmosis units for treatment of pulp and paper mill effluents were realized. The most obvious is that adequate prefiltration of the feed must be provided to prevent fiber accumulation from shutting the units down. The outside-flow type tube bundle could only be practical when such pretreatment is used, because even if the tubes did not break, the flow through a clogged bundle would be drastically altered. The use of an inside-flow tubular membrane support would be advisable if the porous tube material is suitable for dynamic membrane formation and can withstand the high internal pressure. This configuration would lessen the probability of fibers and solids accumulating on membrane surfaces, and a smooth continuous membrane could be formed more easily. The use of a pH control system was found to be unnecessary because the waste water pH did not go much higher than 10.0.

The rejections of the various parameters indicate that this type of membrane system could be developed to concentrate decker filtrates, or other waste waters containing pulping chemicals, to produce solutions concentrated enough for economical recovery of chemicals. The large organic molecules which contribute to color were removed almost entirely, and sodium and total sulfur rejections were also high (see Table 6). The chlorides were rejected well, but the actual chloride concentration was low and not a major concern. The BOD_5, COD, and TOC rejections indicate that the permeate should be useable for recycle purposes, especially because the unit can treat hot waste waters.

ULTRAFILTRATION UNIT

As with the reverse osmosis unit, equipment malfunctions and processes with the membrane support system (piping and tube bundles) prevented the accumulation of data which could be reliably used for scale-up purposes. However, the pilot operations that were performed provided information which will be invaluable for future work with dynamic membranes. The data from the six ultrafiltration runs are summarized in Table 15 and are indicative of the differences in operation. Run U-1 was the best with regard to rejection of solutes at high flux rates. Runs U-2 and U-3 had good color rejections but poor solids rejections and also poor flux rates. Run U-4, the first trial with the carbon tubes, obtained better fluxes with fairly good color removals but only fair total solids rejection. The fair to good rejections of TOC, COD, and BOD_5 indicated, in conjunction with the previous statement, that the unit was rejecting the large organic molecules which comprise the color bodies, while the smaller organics were allowed to pass through. Runs U-5 and U-6 started poorly, but membrane washes and extra layers of membrane improved both fluxes and rejections to a level approaching those of Run U-1. In the last day of Run U-5, the fluxes and rejections from individual ceramic tube bundles were determined. The data for these bundles are given in Table 16. The tube bundles did not show any distinct trends regarding flux vs. rejection, nor did any trends become evident in the position of a single bundle in the series. This randomness and the previous problems with the bundles in this run indicate that the problems in membrane formation, operation, and clean up are related to individual bundles rather than the system as a whole. This tends to reinforce the concept that dynamic membranes are a viable system and that the problems encountered here were peculiar to this particular unit. If the poor fluxes and rejections were a membrane problem rather than a mechanical problem, one would expect uniformly poor individual performances. If tubes were rubbing each other or the piping, causing uneven membrane formations, one would expect uneven fluxes.

The overall performance when a successful membrane formation (such as that of Run U-1) is completed is very good, with high fluxes and rejection. The membrane will probably need a water rinsing about every 2 weeks, depending on the solids level maintained in the concentrate stream. It is possible to achieve a total solids level of over 10% with this type of system and to then introduce this stream into the mill recovery system. A high level of organics removal with low chloride buildup is possible; this is a desirable feature when treating bleach plant liquors. The color removal is usually quite good even with poor membrane performance.

In addition to these general observations, there were several specific items worthy of notice. The permeate was always dark in color when the unit was first started, whether with a new membrane or after an intermittent stoppage. The permeate would gradually clear up in about 15 to 30 minutes. In Runs U-1, U-5, and U-6, the rejections of total solids, ash, COD, and TOC were always lower during the first day of a run than later days. This tended to support the theory that a lignin-type membrane, formed from wood chemical constituents in the feed, was being formed over the hydrous Zr(IV)-Si(IV) oxide membrane.

TABLE 15. SUMMARY OF ULTRAFILTRATION DATA

% Rejection of	Run U-1	Run U-2	Run U-3	Run U-4	Run U-5	Run U-6
Conductivity	26.0-67.4	24.0-42.9	23.0-24.0	19.7-31.1	17.9-44.4	10.3-35.6
Total solids	56.0-97.7	64.0-86.9	55.3-57.0	52.5-58.6	50.9-94.3	45.6-93.6
Ash	42.1-93.6	39.3-76.6	6.5-19.3	30.7-41.4	31.9-83.5	27.9-80.5
Volatile solids	67.2-98.7	81.7-92.3	72.8-73.1	61.3-85.3	73.3-96.9	69.4-96.7
Color	98.9-99.7	94.3-99.1	94.2-95.8	39.4-98.5	96.7-98.8	96.3-99.3
Chlorides	5.5-23.8	N/A	N/A	10.0-33.0	1.1-39.3	4.4-41.7
Sodium	N/A	N/A	N/A	31.0-61.7	3.8-34.6	31.9-82.0
BOD_5	N/A	N/A	N/A	76.2	72.8-92.8	74.1-92.6
COD	N/A	N/A	N/A	71.1-87.6	82.2-97.7	58.8-97.5
TOC	N/A	N/A	N/A	84.4-92.6	81.8-97.4	82.8-97.1
Total sulfur	N/A	N/A	N/A	37.5-79.4	25.8-92.9	48.3-92.9

Note: N/A = Not Available.

TABLE 16. ULTRAFILTRATION DATA, INDIVIDUAL BUNDLES, RUN U-5, DECEMBER 7, 1977

		Per Cent Rejection								
Bundle[1]	Flux, $m^3/m^2/d$ (gfd)	Total Solids	Ash	Volatile Solids	Color	BOD_5	COD	TOC	Sodium	Total Sulfur
1	3.15 (77.3)	95.6	89.0	97.3	98.4	93.1	96.6	97.6	90.0	5.16
2	5.48 (134.6)	96.1	88.0	98.2	99.6	93.9	98.9	98.7	88.3	5.16
4	2.98 (73.2)	94.3	88.2	96.5	98.4	92.2	97.8	97.2	85.1	93.6
5	4.72 (115.9)	94.5	85.2	97.0	98.6	92.2	97.7	97.4	85.2	N/A
6	4.14 (101.7)	95.6	88.1	97.6	99.1	93.3	98.5	97.9	87.9	12.9
8	4.25 (104.3)	95.2	88.1	97.1	98.8	91.9	98.2	97.3	87.4	N/A
9	3.95 (97.0)	94.1	85.9	96.2	98.1	90.8	97.8	96.8	86.0	14.8
10	3.62 (88.8)	94.6	86.5	96.7	98.8	91.1	98.1	97.5	85.3	N/A
11	2.98 (73.2)	94.4	87.5	96.1	98.6	90.3	97.8	97.2	85.1	N/A
12	6.29 (154.5)	94.9	85.0	97.5	99.4	91.9	98.9	98.0	85.4	N/A
13	4.25 (104.3)	93.2	81.0	96.4	97.6	86.9	97.4	96.6	83.0	N/A
14	1.89 (46.4)	93.8	83.2	96.5	97.4	87.2	97.5	96.6	84.9	N/A
15	3.78 (92.7)	94.8	86.8	96.9	98.4	91.7	97.9	97.4	86.7	N/A
16	3.47 (85.1)	93.2	77.4	97.3	97.3	90.8	97.3	96.3	83.6	N/A
Total combined	4.05 (99.3)	94.2	83.8	96.9	98.4	90.0	97.7	96.8	84.6	N/A

[1] Bundle number indicates position in series sequence of bundles.

Note: N/A = Not Available.

The effect of washing the membrane was noted during several runs. At the end of Run U-1, a water rinse was performed, and this improved the flux from 2.25 $m^3/m^2/d$ (55.2 gfd) to 6.36 $m^3/m^2/d$ (156.1 gfd). Mechanical problems precluded evaluation of the long-term effect of this wash. The tubes in Run U-2 were washed three separate times, but no significant improvement was obtained. The same result was noted in Runs U-3 and U-4, with the conclusion being that a washing sequence will not aid a poor membrane but will restore performance to a good one. When simple washes failed to improve fluxes and rejections, another layer of membrane would sometimes help. This was observed in Runs U-5 and U-6, in which two separate membrane additions improved performance dramatically. This emphasizes a useful feature of dynamic membrane systems in that a membrane can be adjusted if the initial performance is not satisfactory.

An interesting observation is that the membrane used in Run U-1 was 4 months old when the run began. The membrane had been stored by simply filling the unit with deionized water. This indicates that dynamic membrane modules can be generated separately from the ultrafiltration unit and stored until needed. This would allow a great degree of freedom in operation because a faulty module (if the system is so designed) could be isolated, removed, and replaced; and the membrane could be washed and regenerated by the user at his convenience using a small scale unit.

The flux rate in Run U-1 held steady while the total solids concentration in the concentrate stream rose. The flux started to drop slightly when the solids concentration reached 8% or higher, indicating that operation at high solids levels is possible. The pressure drop through the unit leveled off and held steady throughout the run. This conflicted with the usual expectation that the pressure drop would rise in proportion to the increase in solids.

The overall flux rate rose as the temperature got higher until the set point of the temperature control system was reached. This emphasizes an advantage of dynamic membrane systems in that higher temperatures cannot only be tolerated but can produce higher flux rates.

If tube bundles are used with an outside flow arrangement, prefiltration of the feed to remove fibers is absolutely necessary. Fiber clogging the bundles cannot be tolerated. No pH control was needed because the pH of the bleach plant waste waters rarely rose above 10.0.

WATER RECOVERY

In any discussion of the capabilities of a reverse osmosis or ultrafiltration unit, the percent water recovery achieved by the unit is an important consideration. The percent water recovery is defined as:

$$\% R_{H_2O} = \left(\frac{\text{volume of permeate produced/unit time}}{\text{volume of concentrate introduced/unit time}} \right) 100 \qquad (6)$$

and represents a measure of how much of the water fed to the unit is recovered. The use of this parameter is based on a constant membrane surface area and a controlled flow regime to achieve the desired percent recovery. Unfortunately, this was not the case with the units in this pilot operation. The flow was controlled to a rate which would produce the desired flow velocity across the tubes, and it was not adjusted to produce a controlled water recovery as the membrane surface area changed because of tube bundle breakage. The tube bundles broke so frequently that a constant surface area was not possible throughout any particular run, and no reasonable comparison of water recoveries from run-to-run or day-to-day was possible. The runs which gave relatively stable and high fluxes were not comparable with laboratory data because the surface areas changed drastically during the runs. Because flux was reported in terms of volume per unit surface area per day, no indication of the changes in total surface area was apparent. For example, Run H-2 started with 29 bundles and was terminated when only 3 bundles remained in operating condition. Thus, no attempt at presenting water recovery data was made in this report.

ECONOMIC EVALUATION

The primary purpose of this pilot plant project was to develop operating and scale-up data which could be used to design a commercial scale installation for the treatment of pulp mill waste waters. This includes defining certain operational parameters of the units, such as the expected fluxes, membrane life, effectiveness of cleaning procedures, equipment reliability, and long-term operating efficiency of the units. The pilot plant study described in this report failed to define these parameters adequately, and in some instances it stressed that the units needed redesigning. A steady-state flux was not achieved in either unit, although it appears that 1.63 $m^3/m^2/d$ (40 gfd) for the reverse osmosis (hyperfiltration) unit and approximately 4.48 $m^3/m^2/d$ (110 gfd) for the ultrafiltration unit would be about optimum. Membrane life was not defined in either case, because neither unit operated long enough to test this parameter. Some tests of cleaning the membrane were made, but not enough data were available to give any clear indication of cleanability, except that a good membrane could be cleaned significantly by a Na_2CO_3 solution. The reliability of the equipment was poor, although it is important to note that the pilot unit was not a commercial unit and definitely is not indicative of the present state-of-the-art in tubular dynamic membrane units. The data clearly show that no long-term reliability or efficiency can be estimated. Thus, any economic evaluation based on this pilot operation would be speculative, and any scale-up thus derived could be grossly undersized or oversized. Previous studies (26, 41) with textile waste waters have been more successful and have indicated that dynamic membrane systems are competitive with other membrane systems. The dynamic membrane system is being studied further for use with pulp mill waste waters.

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APPENDIX A

PRINCIPLES OF OPERATION

Osmosis is the natural process which occurs when two solutions of unequal concentrations of solute(s) are separated by a semipermeable membrane. The process depends upon the existence of such a membrane, which is capable of allowing the passage of the solvent molecules while retaining the solute molecules. The driving force behind the process of osmosis is the vapor pressure differential between the dilute and concentrated solutions. Thus, passage of solvent molecules through the membrane into the concentrated solution will occur until thermodynamic equilibrium is reached or until an external force interferes before the system reaches the lowest chemical potential. The osmotic pressure (π) is the pressure which must be applied to the concentrated solution to prevent passage of the solvent molecules through the semipermeable membrane. The osmotic pressure of a solution is dependent upon the solute concentration, activity coefficient, the degree of ionization of the solutes, and the temperature. It is defined as

$$\pi = iRTC \qquad (1)$$

where π = osmotic pressure, atm

i = van't Hoff's factor, which is dependent upon the activity coefficient and the degree of ionization

R = gas constant = 82.1 atm cm^3/g-mole °K

T = temperature, °K

C = concentration of solute, g mole/cm^3

For an ideal dilute solution, i is a constant, so that the osmotic pressure (π) is directly proportional to temperature and concentration. For pure water, π is equal to zero (6).

Reverse osmosis is the reversing of the natural process by applying an external driving force to overcome the existing osmotic pressure. If a pressure (P) which is greater than π, is applied to the more concentrated solution, the solvent will flow from that side through the membrane into the dilute solution. For any given membrane, the amount of water flowing opposite to the osmotic flow is directly proportional to the differential applied pressure. This flow is measured in terms of volume per unit surface area of membrane and is defined as

$$J = A(\Delta p - \Delta\pi) \qquad (2)$$

where J = flux rate through the membrane, gfd

A = water permeability coefficient, gfd/psig

Δp = difference between the applied pressure and the delivery pressure of product water, psig

$\Delta \pi$ = (difference between the liquor and product osmotic pressures) + (osmotic pressure increase because of fouling and concentration polarization), psig

The product water is delivered at atmospheric pressure, and the osmotic pressure of the product water is very small compared with that of the liquor. Assuming no fouling and concentration polarization effects, the driving force ($\Delta p - \Delta \pi$) becomes equal to the difference between the applied driving force, P_A, and the osmotic pressure of the liquor (π). Then Equation 2 becomes

$$J = A(P_A - \pi) \tag{3}$$

As seen in the Equation 3, as the liquor becomes more concentrated, the osmotic pressure increases, and higher applied pressures are necessary to maintain the flux rate, J.

Although both reverse osmosis and ultrafiltration are processes which involve transport of solute molecules through a semipermeable membrane by applying pressure, the mechanisms, capabilities, and results from the two are quite different. The main differences are the membranes used (and the subsequent mechanism involved), the operating pressure, the size and types of solutes which can be removed, and the quality of the permeates. The membranes used for ultrafiltration are "loose" membranes, meaning that they retain only the higher molecular weight organic molecules. The pore diameters are in the range of 2×10^{-8} to 1×10^{-5} meters (200 to 100,000 angstroms). The membranes used for reverse osmosis are "tighter" and retain low molecular weight organic molecules and inorganic salts. The reverse osmosis membranes are generally asymmetrical, with a macroporous substructure and a dense surface layer. The mechanisms of removal in both reverse osmosis and ultrafiltration are similar in that they both involve a rejection of solute molecules by a semipermeable membrane under the driving force of applied pressure. However, the ultrafiltration process, which operates in a low pressure range of 3.5×10^5 to 2×10^6 Pa(50-300 psi), is a simple sieving operation, separating the solute molecules because of their size or shape. Reverse osmosis, which operates in a pressure range of 1.4×10^6 to 1×10^7 Pa(200-1500 psi), removes solutes mainly by surface interaction between membrane and solute, and to a lesser degree, by physical sieving.

The mechanism involved in reverse osmosis is not fully understood, and two main schools of thought exist. The solution-diffusion theories are based on the concept of the water and any solute molecules which are capable of hydrogen bonding being bonded to available hydrogen bonding sites within the membrane and subsequent transport occurring because of diffusion. Reid and Breton, (1) and Kesting (2) are proponents of this theory but have differing views on the function of the pores in the membrane. Reid and Breton proposed that nonhydrogen bonding species of small enough diameter pass through the pores when the pores are not blocked with bound water, whereas Kesting advocated the view that the pores are membrane imperfections with passage of solutes being size selective (2). The most widely accepted theory is the preferential sorption-capillary flow mechanism proposed by Sourirajan (3, 4). In this theory, the process is one of adsorbing the solution components onto the membrane surface, and the subsequent transport is a capillary flow phenomenon through the pores. Separation of solvent and solute depends on the chemical affinity of the membrane for the solutes, and the transport rate depends upon the size and number of pores and the applied driving force (5). Another pore theory, proposed by Glueckauf, states that the adsorption is less important than the ionic repulsion which takes place within the pores of a membrane with a low dielectric constant material (5). No one theory is universally accepted because each has its faults, but the Sourirajan preferential sorption-capillary flow seems to be the most widely accepted.

The performance of ultrafiltration and reverse osmosis units is usually defined by the percent rejection of the solute in question and the flux rate through the membrane. The percent rejection is defined by

$$\% R = \left(1 - \frac{C_P}{C_F}\right) \times 100 \qquad (4)$$

where $\% R$ = percent rejection

C_P = concentration of the permeate

C_F = concentration of the feed to the module

The % R is affected by many factors, such as the polarity of the membrane, steric effects, ionization and hydration of the solutes, pH, applied pressure hydrogen bonding, and the valence (if removing electrolytes). The more nonpolar a membrane is the better the rejection, because there is less chemical affinity for the membrane by the solute (8). Steric effects are caused by the resistance to transport through the pores because of the size or shape of the molecule to be removed. High molecular weight organic molecules are often too large to fit through the pores. Compounds with the same molecular weight but different configurations are often removed to different degrees. For example, a branched alcohol is removed more completely than a straight chain alcohol, and secondary amines are removed more completely than primary amines. The pH and degree of ionization together can radically affect removals. At a pH where the molecule is only partially dissociated, removals can be markedly lower than if the molecule is completely dissociated (3, 7, 8, 10). Usually there is a linear improvement in rejection with the degree of dissociation (8, 9). The separation of formic acid has been reported at 6% when partially dissociated and up to 98% when fully dissociated (9). The importance of the hydrogen bonding ability of the solute has been recognized, in that molecules which can form hydrogen bonds permeate through the membranes more readily than those which cannot, giving lower rejections (2, 3, 7, 11). The enthalpy of hydration of inorganic ions is recognized as a factor in rejection. The higher the enthalpy of hydration, the bulkier the ion-bound water complex, and the steric effects again become important (9, 12). It has also been found that the rejection of electrolytes increases with valence, with bivalent and trivalent ions being rejected more than monovalent ions. The rejection is also known to improve with increasing pressure, although this effect is more pronounced with solutes which are otherwise poorly removed (8, 13). The main restraints on applied pressure are the mechanical strength of the membrane supports and the adverse effect of membrane compaction, which tends to reduce the flux rates (13).

The flux rate through the membrane is critical to the design of the equipment because it determines the total surface area of membrane necessary for efficient operation. The flux rates for ultrafiltration units are fairly high, usually ranging from 2 to 6 $m^3/m^2/d$ (50 to 150 gfd).

Reverse osmosis units tend to have low flux rates, usually ranging from 0.4 to 1 $m^3/m^2/d$ (10 to 25 gfd). Several of the factors which affect rejection also affect the flux rates. The polarity of the membrane inversely affects flux compared with rejection in that the more nonpolar the membrane, the lower the flux. As shown in Equation 3, flux rates should increase with higher pressures up to the previously mentioned membrane compaction point (13, 14). It is possible to attain higher flux rates by raising the operating temperature, but this is limited by the type of membrane used. The most important factors in maintaining high flux rates are prevention of fouling and concentration polarization. Fouling is a phenomenon which is not well defined but is unique in each situation. Essentially, in many waste-water treatment operations there are constituents in the feed which adversely affect performance by adhering to the membrane surface and lowering the flux rates and in some cases the rejections.

Concentration polarization is a phenomenon which occurs when the concentration of solute on the feed side membrane surface increases to the point that a concentration gradient between the membrane and the bulk solution develops (4, 6, 14, 15, 16). This causes a flux decline because the diffusion of solute away from the membrane surface cannot remove the buildup of a boundary layer. The concentration polarization ratio is defined as (14)

$$CP = \frac{C_M}{C_B} \qquad (5)$$

where CP = concentration polarization ratio

C_M = solute concentration at the membrane

C_B = bulk solute concentration

As the boundary layer builds up, the ratio increases and the osmotic pressure is higher. As a result, the driving force is lowered, unless the applied pressure (P_A) is increased proportionately. For example, a unit operating at 6.89×10^6 Pa (1000 psi) treating a solution containing 35,000 mg/1 total dissolved solids (CP - 1.2, osmotic pressure 2.4×10^6 Pa[350 psi]) has a boundary concentration of 42,000 mg/1 total dissolved solids, with an osmotic pressure of 2.9×10^6 Pa(420 psi). If the feed rate is slowed down to obtain higher water recovery so that the boundary concentration increases 100%, the osmotic pressure is then 4.8×10^6 (700 psi). Thus, instead of a driving force of 1000 - 420 = 580 psi, it is now 1000 - 700 = 300 psi (13).

Another type of fouling occurs when the boundary layer becomes supersaturated with soluble inorganic salts, which precipitate out of solution and plug the membrane. The result is a loss of flux and possible damage to the membrane (14).

It is often possible to avoid the effects of fouling, concentration polarization, and scaling by altering the method of operation and/or redesigning the modules which house the membranes. Fouling can be avoided or lessened by pretreating the feed to remove the fouling components or providing enough velocity to flush fouling layers from the membranes. Separate washings and "pausing" techniques which allow the natural osmosis process to flush out the membrane are also helpful. To eliminate concentration polarization, it is necessary to prevent the formation of the boundary layer by using high velocity flow over the membrane, or by designing the modules to produce adequate turbulence. Scaling can be prevented by pretreatment, pH adjustment, or by keeping the product-to-feed ratio low to ensure that the supersaturated layer does not form (19).

APPENDIX B

MEMBRANE SUPPORTS

In the design and operation of reverse osmosis and ultrafiltration units, the two most important choices to be made are those of the proper membrane material and the most efficient membrane support system. There are four main types of membrane supports: plate and frame, spiral wound, hollow fiber, and tubular. Each has its variations, relative advantages, and disadvantages.

Plate and Frame

These modules consist of flat membranes supported by porous plates and assembled in a stack of closely spaced plates. The feed flows over the membrane and the permeate is drawn off through the porous plates. The permeates can be collected with either a central tube running through the centers of the plates, or with individual tubes at the edge of each plate (17, 18). The plates are closely spaced to prevent laminar flow, and turbulence promoters are used to help control fouling.

Spiral Wound

The spiral-wound module is a unit in which two flat membranes, separated by a porous support, are wrapped around a porous collection pipe like a jelly roll. The edges of the two membranes are sealed together, and a spacer is provided between the membrane surfaces to allow axial flow of the feed. The permeate flows through the porous support to the central collection pipe (19, 20).

Hollow Fiber

This system consists of thousands of very fine hollow fibers made of the membrane material itself. The earliest models used external feed flow, in which a bundle of hollow fibers was folded double and the open ends set in a bonding resinous material. The feed flowed under pressure over the outside of these fibers, and the permeate passed out the ends of the fibers for collection. More recently, fibers have been developed which allow internal feed flow through the fibers. This has an advantage over the outside flow as this configuration is less likely to foul and easier to backwash (20, 21).

Tubular

This module consists of a membrane applied either on the inside or outside of a porous tube. The feed flows tangientially over the membrane and the permeate is collected on the other side of the tube wall. Various materials have been used for the porous tubes: spiral-wound fiberglass, carbon, stainless steel, ceramic, and thin polymeric tubes encased in sand (for strength) (6, 22, 23, 24, 25).

Comparison

Several studies have been performed in which two or more of these module types were operated and compared (2, 6, 9, 21, 24, 26, 27, 28). Each configuration has its own intrinsic advantages and disadvantages. The proper choice of a membrane support is a balance of efficiency and economy.

The plate and frame configuration was the first to be used in large scale reverse osmosis applications. The system requires large equipment, high maintenance costs, and a large space for the equipment installation. This module is more prone to foul than others, and damaged membranes are more difficult to replace than with the other units. These units are presently being marketed in an improved version, but use of plate and frame systems is not yet widespread (17, 18).

The spiral-wound module has a large total membrane surface area per unit volume of equipment, good production efficiency, and low cost per gallon of water (permeate) produced. The early models had problems with fouling, plugging, bad flow distribution, and poor overall reliability (19). The recently developed modules, spacers, turbulence promoters, and new designs have improved performance, and the fouling and plugging problems are minimal and cleaning is easier. Even so, if the feed contains fibers, suspended solids, or other debris, pretreatment is necessary. The closely spaced flow channels will not allow the treatment of viscous liquids. The high pressure drop through these modules necessitates the use of auxiliary pumping to repressurize the feed between modules (20). If conditions permit, spiral-wound modules are preferred over tubular units because this configuration has larger membrane surface area and productivity (20, 27).

The hollow fiber module gives the highest productivity and lowest basic equipment cost because it has the highest surface area per unit volume of any of the modules (1, 19, 26). The basic equipment cost is low because the individual fibers can withstand the high pressure without support and are simply encased in a pressure vessel. However, this configuration is the most susceptible to fouling and concentration polarization, and the external flow type is the hardest to to clean (9, 20, 21). The units cannot be used to treat viscous liquids, or those containing suspended solids (unless pretreated). The newer internal flow fibers have a better resistance to fouling and can be backwashed. Hollow-fiber modules are most widely used for demineralization, rather than waste-water treatment.

Tubular modules are an attempt to solve operational problems at the expense of overall cost and efficiency. Tubular systems, both internal and external flow, give fluxes and rejections comparable with spiral-wound and hollow-fiber modules, but the productivity per unit volume at conventional fluxes is much lower because of the much smaller surface area per unit volume (20, 24). Tubular units are the best choice for viscous liquids, and their operation can be adjusted to reduce the effects of fouling, plugging, and concentration polarization. Cleaning is easiest with tubular units and higher pressures in the range of 2.8×10^6 Pa (400 to 1500 psi) can be used, as opposed to 2.8×10^6 to 4.1×10^6 Pa (400 to 600 psi) with spiral-wound or hollow-fiber units. The tubular units need the least, if any, pretreatment of feeds but require substantially larger capital outlays because they are the most expensive to fabricate and to install.

Thus, the choice of module depends heavily upon the intended applications, productivity requirements, space limitations, and pretreatment capabilities. The lower cost and higher productivity of spiral-wound and hollow-fiber units may be offset by the cost of pretreatment to prevent fouling and plugging of these units. Treatment of a viscous feed with a high suspended solids concentration precludes any but tubular units. It is also possible that extreme pH conditions could eliminate any of the available membranes, except the inorganic tubular varieties. The module-type choice is an important consideration in the design of a waste-water treatment unit.

APPENDIX C

ANALYTICAL PROCEDURES

The following procedures were used to analyze the permeates and concentrates from the pilot plant operation:

Total Solids: Standard Methods[1], section 208 A, pp. 91-92

Total Volatile Solids: Standard Methods, section 208 E, p. 95

Ash: Standard Methods, section 208 E, p. 95

Chemical Oxygen Demand: Standard Methods, section 508, pp. 550-554

Bio-Chemical Oxygen Demand: Determined by Vester J. Thompson Jr., Inc. (Chemical, Materials and Geothermal Laboratories), 3707 Cottage Hill Road, Mobile, Alabama. The Standard Methods procedure plus a YSI Model 54 RC dissolved oxygen meter was used.

Color: NCASI Procedure[2]

Total Organic Carbon: Measured on a Beckman 915 A Total Organic Carbon Analyzer plus a model 865 Infrared Analyzer. The only pretreatment was dilution.

Sodium: Determined on a Perkin-Elmer model 303 Atomic Absorption Spectrophotometer with flame emission attachment. The pretreatment was to dissolve the weighed sample of liquor in 2 ml. concentrated hydrochloric acid and demineralized distilled water as needed. The resulting solution was filtered into a 100-ml. volumetric flask using qualitative filter paper. Filter paper and container were washed several times with water. The solution was diluted to the mark with demineralized distilled water. If the resulting solution was too concentrated for analysis, an aliquot was diluted to proper strength with demineralized water.

Total Chloride: Determined by Galbraith Laboratories, Inc., Knoxville, Tennessee

Total Sulfur: Determined by Galbraith Laboratories, Inc., Knoxville, Tennessee

[1] *Standard Methods for the Examination of Water and Waste Water.* American Public Health Association, *et. al,* Fourteenth Edition, Washington D. C., 1976.

[2] *An Investigation of Improved Procedures for Measurement of Mill Effluent and Receiving Water Color,* Stream Improvement Technical Bulletin. No. 253. National Council of the Paper Industry for Air and Stream Improvement, Inc., New York, New York, 1971.